Practical Guide to Interpretive Near-Infrared Spectroscopy

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Lois Weyer

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Cover graphic (arbitrary absorbance scaling). This graphical representation of a near-infrared spectrum indicates the 8 (eight) locations (shown using small blue arrows) representing C-H stretching information for 2, 2, 4-trimethyl pentane. The spectrum extends from about 690 nm to 3000 nm (14,493 cm\(^{-1}\) to 3333 cm\(^{-1}\)). When viewing the near-infrared spectrum from right to left one observes the fundamental (\(\nu\)) combination region where a significant quantity (high rank) of molecular vibrational information is found; then the first overtone (2 \(\nu\)) C-H stretching region (section 2); the first overtone (2 \(\nu\)) combination region (section 3); the second overtone (3 \(\nu\)) C-H stretching region (section 4); the second overtone (3 \(\nu\)) C-H combination bands (section 5); the third overtone (4 \(\nu\)) C-H stretching region (section 6); the third overtone (4 \(\nu\)) combination bands (section 7); and finally the fourth overtone (5 \(\nu\)) C-H stretching region (section 8).
Dedication

To the ones that have gone before us and upon whose work our work is based
To the ONE who so marvelously engineered this universe of mystery, symmetry, and magnificent order.

Jerry Workman

To the supportive and inspiring teachers and professors, including Tom Medwick, Phyllis Dunbar, Barbara Irwin, Steve Brown.
To Steve Prescott, who let me take background materials home.
To Dorothy Tunstall for past help, and Linda Perovich for current assistance.
To encouraging friends including Howard Barth and many in the NIR community.
To Dorothy Delker, Caroline Herschel, and the rest of the many female scientists of the past and present.
To the women in the Hercules Library, past and present.
To my family members, especially Gordon, Geoff, and Nathan.

Lois Weyer
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Preface

Qualitative and quantitative near-infrared (NIR) spectroscopic methods require the application of multivariate calibration algorithms commonly referred to as chemometric methods to model spectral response to chemical or physical properties of a calibration, teaching, or learning sample set. The identification of unique wavelength regions where changes in the response of the near-infrared spectrometer are proportional to changes in the concentration of chemical components, or changes in the physical characteristics of samples under analysis, is required for a scientific understanding of cause and effect, even for routine method development.

The first step to developing an analytical method using NIR is to measure a spectrum of the sample using an NIR spectrophotometer. It is helpful to note that the near-infrared spectrum obtained by using a spectrophotometer is the result of the convolution of the measuring instrument function with the unique optical and chemical characteristics of the sample measured. The sample participates as an optical element in the spectrometer. The resultant spectrum contains information specific to the molecular vibrational aspects of the sample, its physical properties, and its unique interaction with the measuring instrument. Relating the spectra to the chemical structure of the measured samples is referred to as spectra–structure correlation. This correlation or interpretation of spectra converts the abstract absorption data (spectrum) into structural information representing the molecular details about a measured sample. Interpretive spectroscopy of this sort provides a basis for the establishment of known cause-and-effect relationships between the spectrometer response (spectrum) and the molecular properties of the sample.

The exclusive use of chemometrics alone provides a weak basis for analytical science. When performing multivariate calibrations, analytically valid calibration models require a relationship between X (the instrument response data or spectral data) and Y (the reference data); probability tells us only if X and Y “appear” to be related. If no cause–effect relationship exists between X and Y, the analytical method will have no true predictive significance. Interpretation of NIR spectra provide the knowledge basis for understanding the cause-and-effect of molecular structure as it relates to specific types of absorptions in the NIR. Interpretive spectroscopy is a key intellectual process in approaching NIR measurements if one is to achieve an analytical understanding of these measurements. This book represents our best effort to provide the tools necessary for the analyst to interpret NIR spectra.

Although there have been no books written specifically on the interpretation of NIR spectra, a number of classic reviews have been published. A few of these have included charts or spectra showing specific band absorptions.

The most important early reviews covered the 1920s through the 1950s, a time when new commercial UV-Vis-NIR instruments became available and interest in the spectral region increased in both academia and industry. These included reviews by Wilbur Kaye of Tennessee Eastman, Owen Wheeler of the University of Puerto Rico, and Robert Goddu of Hercules Powder Company (now Hercules Incorporated). In addition, Wheeler cited an earlier review by Joseph W. Ellis summarizing NIR papers published before 1929, and Lauer and Rosenbaum reviewed band assignments in 1952.

Wheeler’s article includes a table of approximate theoretical wavelengths of overtones, such as the C–H stretch first overtone at 1.7 microns, the second overtone at 1.1 microns, the third at 0.85, and the fourth at 0.7. Kaye’s 1954 article provided a chart of the spectra-structure correlations and approximate absorptivities that were available at that time. The same article also provided very detailed band assignment tables and spectra for a few specific compounds. In 1960, Goddu and Delker
published a more complete chart that has been widely reproduced. It was based on literature references and personal knowledge from a series of studies and publications.

During the 1960s and 1970s, NIR was not studied as extensively, although another important review was written by Kermit Whetsel in 1968 and some work did continue at specific institutions. A chapter on NIR interpretation was included in Robert Conley’s text on infrared spectroscopy published in 1966. This was the time period in which Karl Norris at the USDA began his research that would lead to the greatly renewed interest in this spectral field, but there was initially a disconnect between the new agricultural applications of NIR and the earlier academic and chemical industry interests.

There were some specialized reviews during this time period. For example, reviews on hydrocarbon NIR spectra were written by Bernhard and Berthold, and Tosi and Pinto. An atlas of 1000 NIR spectra of a wide selection of general chemicals was published in 1981. Although the spectral bands are not interpreted, the atlas provides an excellent reference collection.

As the new rapid scan, optically optimized instruments became popular in the food and agricultural industries and began to be noticed by other industries, several reviews were written to bridge the knowledge gap. These include those by Weyer, Honig, and Stark, Luchter, and Margoshes. An important book, first published in 1987 by Norris and Williams, has a chapter on chemical principles, including band assignments. There is also interpretive information in Osborne and Fearn’s food analysis book. More recent extensive reviews on spectral interpretation include those by Workman and Weyer and Lo.

The shortwave near-infrared spectral region was specifically discussed by Schrieve et al. They referred to synonyms such as “the far-visible,” the “near, near-infrared,” or the “Herschel infrared” to describe the range of approximately 700 to 1100 nm of the EMS (electromagnetic spectrum). The authors cite the increased interest of this spectral region to spectroscopists, particularly those involved with implementing process near-infrared measurements. More details regarding this spectral region are also described in a comprehensive handbook by Workman.

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REFERENCES


Introduction to Near-Infrared Spectra

1.1 MOLECULAR SPECTRA

Molecular spectra result from the periodic motions (or vibrational modes) of atomic nuclei within their respective molecules. These nuclei move together or apart along a straight-line vector; and they rotate; they vibrate; they wag; and they bend relative to their centers of gravity. The vibration and bending of molecules exhibit vibrational spectroscopic activity that may be measured using any number of spectroscopic techniques, including the near-infrared, mid-infrared, far-infrared (terahertz), and Raman spectroscopy. The resultant spectra from these molecular vibrational measurement techniques are highly structured and complex. The process of understanding or characterizing this complexity into the spectra–structure correlations for near-infrared spectra is the purpose of this book.

The energy level in a molecule is described as the sum of the atomic and molecular motions due to translational, rotational, vibrational, and electronic energies. Translational energy has no effect on molecular spectra, whereas the other motions do affect the spectral characteristics. Rotational energy is proportional to the angular velocity of rotation for each molecule. Electronic energy in molecules and their various quantum numbers are described via the Pauli principle and are beyond the scope of this work. We will restrict our discussion to the vibrational energy levels and use the application of what is learned in this model as a basis for our specific structure-correlation characterization of near-infrared (NIR) spectra.

1.2 VIBRATIONAL ENERGY LEVELS

Note that a molecule with N atoms has three degrees of freedom for motion (3N). For all three-dimensional objects, there are three axes of translation (x, y, z) and three axes of rotation (as there are three axes of inertia). If we eliminate these six kinds or types of motion (as they are nonvibrational), we are left with 3N-6 vibrational types of motion. (Note: If the molecule is linear like many polymers, there are 3N-5 types of motion.) Each other kind of motion is vibrational in nature and has a specific frequency associated with it. As long as the bonds do not break and the vibrations have motions (amplitudes) of about 10–15% of the average distance between atoms, the vibrations are considered harmonic. Any harmonic is considered to be the superposition of two or more vibrations of the molecule and carries the term normal vibration.

The frequency of any vibration is not dependent on amplitude. The displacement functions for these normal vibrations are described exactly as a sine-wave function. There are 3N-6 normal vibrations in a molecule, and their respective vibrational frequencies are called the fundamental frequencies of the molecule. Symmetry of the molecule is the single factor most important in determining both frequency and amplitude of a molecular vibration. The selection rules discussed later will place a heavy emphasis on symmetry.

1.3 SPECTRAL RESPONSE AND MOLECULAR CONCENTRATION

Harmonic vibrations follow a functional description such that the type of vibration determines the frequency at which it absorbs NIR energy. The amplitude of the absorption at any particular wavelength or wavenumber is determined by its absorptivity and the number of molecules
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encountered within the beam path of the measuring instrument. It is assumed that a change in spectral response is related to a concentration as described by the Bouguer, Lambert, and Beer relationship, most often termed Beer’s law. The Beer’s law relationship is described as: the absorbance (A, AU, or signal strength) of an analyte being measured using a spectrophotometer is equivalent to the product of the absorptivity ($\varepsilon$) of a specific type of molecular vibration; the concentration (c) of the molecules in the measurement beam; and the pathlength (l) of the sample holder within the measurement beam. This relationship between measured spectral signal and concentration of a molecule is most often expressed as

$$A = \varepsilon cl$$

(1.1)

where $\varepsilon$ is the molar absorptivity (referred to as molar extinction coefficient by earlier physicists) in units of liter · mole$^{-1}$ · cm$^{-1}$; c is the concentration of molecules in the spectrometer beam in units of mole· liter$^{-1}$; and pathlength is the thickness in units of centimeters of the measured sample at a specific concentration. The absorptivity for any specific molecule type is calculated by careful measurements of the absorbance of a compound generally diluted in a suitable organic solvent, and by applying the relationship

$$\varepsilon = \frac{A}{cl}$$

(1.2)

Note that for transmittance (where $T = 0.0–1.0$) and percent transmittance (where $T = 0–100.0$) spectroscopy, a more complete delineation of the relationships between the various terms is contained in an expression such as

$$T = \frac{I}{I_0} = 10^{-\varepsilon cl} \Rightarrow \text{Abs.} = A = -\log_{10} \left( \frac{I}{I_0} \right) = -\log_{10} T = \varepsilon cl$$

(1.3)

Here the symbols $I$ and $I_0$ represent the attenuated energy detected after sample interaction and the initial energy incident to the sample, respectively. For reflectance (where $R = 0.0$ to $1.0$) and percent reflectance (where $R = 0.0$ to $100.0$) spectroscopy, the various relationships are expressed as

$$R = \frac{I}{I_0} = 10^{-\varepsilon cl} \Rightarrow \text{Abs.} = A = -\log_{10} \left( \frac{I}{I_0} \right) = -\log_{10} R = \varepsilon cl$$

(1.4)

The relationship where the change in intensity (I) of the transmitted or reflected light from a sample is a function of the change in pathlength (l) of the sample as expressed by the absorptivity ($\varepsilon$) of a specific analyte (or molecular substance) and its concentration (c) is denoted by

$$-\frac{\partial I}{\partial l} = \varepsilon cl$$

(1.5)

Modern spectrophotometers utilize these assumptions for making spectroscopic measurement and generally display spectroscopic data as transmittance (T), reflectance (R), and absorbance A (y-axis or ordinate axis), versus wavelength (nanometers, microns) or wavenumber (cm$^{-1}$) (as x-axis, or abscissa axis).
1.4 NOMENCLATURE OF MOLECULAR VIBRATIONS

There are multiple types of molecular vibrations that absorb at unique wavelengths or frequencies of near-infrared energy depending upon the bond type. Several normal (or normal mode) types of molecular vibrations active within the NIR region are illustrated in the following figures. Each of these types of vibrations has a unique frequency where absorption occurs. The location of these frequencies and the associated molecular structures (spectra-structure correlations) are the purpose of this book.

1.5 STRETCHING VIBRATIONS

Common nomenclature used in near-infrared spectroscopy indicates that such molecular vibration is a variation of the length of the bond and is indicated by the symbol $\nu$. If the group consists of three atoms, instead of two, it can have two types of stretching: asymmetric and symmetric. In order to distinguish the two types of stretching, a subscript is introduced: “s” (for symmetrical stretching) and “a” (for asymmetrical stretching). Figures 1.1 through 1.6 demonstrate stretching vibrational motions in C–H-containing molecules.
FIGURE 1.3 Methylene symmetrical stretching of $\text{CH}_2 \rightarrow \nu_s$. (In this movement the two hydrogen atoms move away from the carbon atom at the same time in the outward movement and approach each other at the same time in the return movement.)

FIGURE 1.4 Methylene asymmetric stretching of $\text{CH}_2 \rightarrow \nu_a$. (In this movement, while one hydrogen is moving away from the carbon atom, the other is approaching it.)

FIGURE 1.5 Symmetrical stretching of $\text{O}–\text{C}–\text{H} \rightarrow \nu_s$. (In this movement, the two hydrogen atoms move away from the carbon atom at the same time in the outward movement and approach it at the same time in the return movement.) The oxygen atom is moving in a likewise external direction as the hydrogen atoms with respect to the carbon atom.
1.6 BENDING

This is a variation or change in the angle of a bond occurring on the plane of the bond as indicated with the symbol $\delta$. Figures 1.7 through 1.10 show bending molecular motions.

If the molecular group consists of four atoms (e.g., one carbon and three hydrogen atoms), instead of three (e.g., one carbon and two hydrogen atoms), they can have two types of bending: symmetrical and asymmetrical.

Symmetrical bending is indicated by adding the subscript $s$, and asymmetric the subscript $a$.

In symmetrical bending (Figure 1.10), the angle $4\rightarrow1\rightarrow3$, the angle $4\rightarrow1\rightarrow2$, and the angle $3\rightarrow1\rightarrow2$ are increased at the same time in the outward movement, and are tightened at the same time in the return movement. This is a movement that simulates the opening and closing of an umbrella; it is also called umbrella bending.

In asymmetric bending, one of the three angles is tightened (in the outward movement), and the other two are increased; and vice versa in the return movement.\(^1\)

FIGURE 1.6 Asymmetric stretching of O–C–H $\rightarrow \nu_c$. (In this movement, while one hydrogen atom moves away from the carbon atom, the other two approach it.) In the second type of asymmetrical motion, two hydrogen atoms move away from the carbon atom while the other moves toward the carbon atom.

FIGURE 1.7 Methylene bending of CH$_2$ $\rightarrow \delta$. The two methylene hydrogen atoms move toward each other or away from each other simultaneously.
FIGURE 1.8 Methyl symmetrical bending of CH$_3$ → $\delta_s$.

FIGURE 1.9 Methyl asymmetric bending of CH$\rightarrow$ $\delta_a$.

FIGURE 1.10 Internal umbrella (symmetrical) bending motion of tetrahedron CH$_3$. 
1.7 BEGINNING GROUP THEORY FOR NEAR-INFRARED SPECTRA

Group theory is used to solve problems in chemistry specifically related to the symmetry properties of a molecule. Near-infrared absorption bands are described using the vibrational energy of the molecules measured. Molecular motion relative to the atomic nuclei is described using the x, y, z (Cartesian) coordinate system; for each atom there are three degrees of freedom for the motions allowed. If we have N atoms, then there are three times N degrees of freedom. A more useful way to describe the coordinate space of molecules is by the use of group theory. Group theory requires some basic mathematics and an understanding of the modern theories of the three-dimensional shape of molecules. Symmetry can be surmised to have an effect on the energy levels of a molecule simply by examining its spectrum. This applies to infrared, Raman, far-infrared (terahertz), near-infrared, and $^1$H-NMR spectra.

It is not very satisfying nor quantitative to argue that the hydrogen atoms in a symmetrical molecule are all in the same “chemical” or atomic/molecular environment and thus all should “look” the same spectrally. This is certainly true but neither precise nor informative. The rules of symmetry can be precisely and mathematically described, and this is the object of group theory in its application for prediction of spectroscopic complexity based on energy levels. The first concepts and terms that will help to introduce group theory include rotational axes, reflection planes, inversion centers, improper rotational axes, and point groups. The symmetry of a molecule can be described in mathematical notation in terms of its symmetry operations. Excellent references describing group theory include Reference 2 and Reference 3.

1.8 ROTATIONAL AXES

Operations of rotation about an axis, represented by a central atom in a molecule, are an important concept in group theory. A completely symmetrical molecule can be rotated 180 degrees about its central axis and produce a molecule that is “indistinguishable” from its original; a 360-degree rotation produces an “identical” molecule. Note that this indicates that labeled molecules would be in different positions relative to a fixed observer for the 180-degree rotation, and be in identical positions for two successive 180-degree rotations. The order of these rotational axes are represented mathematically by the ratio of 360/r, where r is the number of degrees of rotation around an axis that produces an indistinguishable molecule. For example, an $\text{Sp}^3$ molecule requires a 120-degree rotation along the long axis of the molecule and is thus 3rd-order; a molecule such as cyclohexane or benzene, when rotated around its principal axis (the axis perpendicular to the plane of the molecule), would require a 60-degree rotation and therefore has an order of 6.

1.9 REFLECTION PLANES

The concept of reflection planes refers to symmetry assessed using the mirror-image approach: an imaginary double-sided mirror is used to bisect the molecule along various planes, and the reflection from each side of the mirror is used to reconstruct the other side of the molecule. Thus, once this mental reconstruction or visualization of the molecule is completed, a symmetrical molecule will be indistinguishable from the original when using this method.

1.10 INVERSION CENTERS

Inversion centers, referred to as $i$, are another instrument for demonstrating the symmetry of a molecule. Unlike the Rotational and Reflection methods for which a molecule may have many axes or planes, there is only one inversion center per molecule. For this exercise to test symmetry, imagine...
that each molecule has a center of mass with bonds at opposite ends of the molecule. If the atoms at the ends of these bonds are inverted or switched with one another, does the inverted form of the molecule remain indistinguishable as compared to the original? If so, the molecule is symmetrical.

1.11 IMPROPER ROTATIONAL AXES

This is a symmetry operation needed on a molecule where one of the atoms lies along the rotational axis and cannot be transformed into the position of other atoms on the molecule simply by rotation or reflection methods. In this case, the improper rotation axis must be used to bring this atom into the position of other atoms so it can be transformed (by rotation or reflection) into the position of the other atoms. Methane can be used as an example molecule.

1.12 POINT GROUPS

The point group system is a formal nomenclature method for designating symmetry operations. Point indicates the single point in space that each symmetry operation passes through; this can be either a central atom within a molecule or a center of mass for a molecule without a central atom. The term group indicates a group of symmetry operations around the designated point. There is a set of symmetry rules that are used to classify a molecule by point groups.

1.13 DEFINING A GROUP USING MATRIX OPERATIONS

A group for this discussion may be described as a formation of atoms interacting as a molecular association and having a common set of rules whereby motion is allowed under specific prescribed conditions. There are verbal descriptive definitions for such groups, but mathematics provides a precise description. The mathematics used include the use of basic matrix algebra. Some definitions are useful: an identity operation is the result of a combination of events; a combination of events follows associative properties (in a mathematical sense); and there is an inverse operation for all events. So, to give mathematical definitions for these terms using matrix notation is extremely useful. Matrix multiplication is also used because of its importance in describing group interactions.

All molecules have symmetry elements in their structures. These structures have only certain potential motions allowed around any particular plane or rotational axis. For example, with crystal structures, there is a limit of 32 possible combinations of symmetry elements (or motions) allowed. These individual allowed motions are also termed point groups. There are 32 groups, plus some additional groups that have specific axes of symmetry, for most molecules. Each of the groups has specific names and prescribed motions. These possible rotational motions are represented or expressed in matrix notation and described by using the standard matrix operations shown in the following text. The reader is referred to Chapter 3 and Chapter 14 of Reference 2 (Colthup, Daly, and Wiberley’s classic infrared text) for a thorough explanation. A separate source providing a working tutorial on the subject is found in Reference 3 (Walton). Walton summarizes group theory with eight points, noting that symmetry elements are comprised of rotational axes, reflection planes, inversion centers, and improper rotation axes as illustrated by the characters in Figure 1.11. More details and descriptions of these molecular properties are to be found in Reference 2 and Reference 3.

1.14 PRACTICAL ASPECTS FOR SPECTRAL MEASUREMENTS

A variety of sample presentation methods are available to the analytical scientist. These include transmittance (straight and diffuse), reflectance (specular and diffuse), transflection (reflection and transmittance), and interactance (a combination of reflectance and transmittance). Pathlength selection
Introduction to Near-Infrared Spectra

for optimum near-infrared measurements involves the following: for the shortwave near-infrared (SW-NIR) region of 12,500 to 9091 cm\(^{-1}\) (800–1100 nm), pathlengths ranging from 5–10 cm are typically used. For longwave near-infrared (LW-NIR) or 9091 to 4000 cm\(^{-1}\) (1100–2500 nm), common pathlengths for hydrocarbons include 0.1–2 cm or 1–20 mm.

The sample presentation geometries most often used in near-infrared measurements are given in Table 1.1. For this table, the abbreviations used designate transmittance (T), diffuse transmittance (DT), and diffuse reflectance (DR). Transmittance and diffuse transmittance are the identical sample presentation geometry, but the sample for DT is a series of particles allowing light to penetrate without significant backscatter. DR is used for samples of infinite optical thickness that will not transmit light if T or DT is used. The ideal surface for DR is a Lambertian or isotropic surface where light is reflected diffusely or evenly throughout a hemisphere above the surface.

Samples exhibit different optical characteristics that must be considered in order to optimize spectroscopic measurement. Standard clear samples or solutions are measured using transmission spectroscopy. Highly colored samples are generally measured using transmission spectroscopy unless the optical density exceeds the linear range of the measuring instrument. At this point, either dilution or reducing the pathlength is preferred.

Fine scattering particulates of 5 to 25 times the measuring wavelength are measured using diffuse transmittance or diffuse reflectance methods. The scattering produced by some of the

---

**TABLE 1.1**

Sample Presentation Methods for Polymers and Rubbers

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Sample Presentation</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquids (lower viscosity)</td>
<td>T and DT</td>
<td>Maintain Instrument within linear measurement range, that is, generally less than 1.5 AU</td>
</tr>
<tr>
<td>Slurries (high viscosity)</td>
<td>T and DT</td>
<td>Maintain Instrument within linear measurement range, that is, generally less than 1.5 AU</td>
</tr>
<tr>
<td>Solids and smaller particles</td>
<td>DR</td>
<td>For DR use infinite optical thickness</td>
</tr>
<tr>
<td>Webs</td>
<td>DR and DT</td>
<td>For DR use infinite optical thickness</td>
</tr>
<tr>
<td>Pellets (large particles)</td>
<td>DR and DT</td>
<td>For DR use infinite optical thickness</td>
</tr>
</tbody>
</table>
reflected light creates a pseudo-pathlength effect. This effect is compensated for by using scatter correction data-processing methods for quantitative measurements, sieving the particles, or grinding to improve particle size uniformity.

Large scattering particulates on the order of 100 times the measuring wavelength in diameter present a challenge for measurements as the particles intercept the optical path at random intervals. Signal averaging can be employed to compensate for random signal fluctuations. Reflection spectroscopy can be used to measure the size, velocity, and concentration of scattering particulates within a flowing stream.

Very high absorptivity (optically dense) materials with absorbances above 4–6 AU are difficult to measure accurately without the use of high-precision photometric instruments, such as a double monochromator system having stray light specifications below 0.0001% T. Measurements can be made with extremely slow scanning speeds and by opening the slits during measurement. These measurements should be avoided by the novice unless high-performance instrumentation and technical support are available. Table 1.2 shows the relative absorption-band intensities for each particular band as well as general spectral windows for fundamental through fourth overtone C–H stretching regions.

### 1.15 TYPES OF NEAR-INFRARED ABSORPTION BANDS

Infrared energy is the electromagnetic energy of molecular vibration. The energy band is defined for convenience as the near-infrared covering 12,821 to 4000 cm\(^{-1}\) (780–2500 nanometers); the infrared (or mid-infrared) as 4000 to 400 cm\(^{-1}\) (2500–25,000 nm; and the far-infrared (or terahertz) from 400 to 10 cm\(^{-1}\) (25,000–1,000,000 nm). Table 1.3 illustrates the region of the EMR (electromagnetic radiation) spectrum referred to as the NIR region. The table shows the molecular interactions associated with the energy frequencies (or corresponding wavelengths) of the various regions.

Specific molecular bonds most active in the NIR are listed here, with X–H bonds being the more active and intense.

- C=O from aldehydes
- C=O from amides
- C=O from carboxylic acids
- C=O from esters
TABLE 1.3
Spectroscopic Regions of Interest for Chemical Analysis

<table>
<thead>
<tr>
<th>Region</th>
<th>Wavenumbers/ (Wavelength)</th>
<th>Characteristic Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultraviolet</td>
<td>52,632–27,778 cm⁻¹</td>
<td>Electronic transitions: delocalized Pi electrons</td>
</tr>
<tr>
<td></td>
<td>(190–360 nm)</td>
<td></td>
</tr>
<tr>
<td>Visible</td>
<td>27,778–12,821 cm⁻¹</td>
<td>Electronic transitions: color measurements</td>
</tr>
<tr>
<td></td>
<td>(360–780 nm)</td>
<td></td>
</tr>
<tr>
<td>Near-Infrared (NIR)</td>
<td>14,493–3333 cm⁻¹</td>
<td>Overtone and combination bands of fundamental molecular</td>
</tr>
<tr>
<td></td>
<td>(690–3000 nm) or 12,821–4000 cm⁻¹</td>
<td>vibrations, especially stretching and bending</td>
</tr>
<tr>
<td></td>
<td>(780–2500 nm)²</td>
<td>(some deformation as well)</td>
</tr>
<tr>
<td>Infrared (IR)</td>
<td>4000–400 cm⁻¹</td>
<td>Fundamental molecular vibrations: stretching,</td>
</tr>
<tr>
<td></td>
<td>(2500–25,000 nm)</td>
<td>bending, wagging, scissoring</td>
</tr>
<tr>
<td>Far-Infrared (FIR or Terahertz)</td>
<td>400–10 cm⁻¹</td>
<td>Molecular rotation</td>
</tr>
<tr>
<td></td>
<td>(2.5 × 10⁶ to 10⁹ nm)</td>
<td></td>
</tr>
</tbody>
</table>

*Official ASTM International Definition.

C=O from ketones
C–H from aldehydes
C–H from alkanes
C–H from alkenes
C–H from alkynes
C–H from aromatic compounds
C–N from amines, alkyl
C–N from amines, aromatic
C–O from alcohols, ethers, and esters
N–H from amides
N–H from amines
NO₂ from nitro groups
O–H from alcohols (no hydrogen bonding)
O–H from alcohols (with hydrogen bonding)
O–H from carboxylic acids

1.16 PROPERTIES OF INFRARED–NEAR-INFRARED ENERGY

Light has both particle and wave properties; quantum theory tells us that the energy of a light particle or photon $E_p$ is given by

$$E_p = hv$$

where $h =$ Planck’s constant (or $6.6256 \times 10^{-27}$ erg-sec), and $v$ is the frequency of light (or the number of vibrations per second or in units of sec⁻¹). Thus, the energy for any specific photon can be quantified, and it is this energy that interacts with the vibrating bonds within near-infrared active molecules. The subsequent values for wavelength, wavenumber, and frequency for both the visible and the extended near-infrared regions are shown in Table 1.4.
1.17 NORMAL MODE THEORY (THE IDEAL OR SIMPLE HARMONIC OSCILLATOR)

Light from a spectrophotometer is directed to strike a matrix consisting of one or more types of molecules. If the molecules do not interact with the light, then the light passes through the matrix with no interaction whatsoever. If molecules interact with the light in a very specific way (i.e., molecular absorption), we refer to them as active or infrared active. For NIR energy, the overtones of X–H bonds, i.e., N–H, C–H, and O–H stretching and bending are of the greatest interest. Infrared active molecules can be seen as consisting of mechanical models with vibrating dipoles. Each dipole model vibrates with a specific frequency and amplitude as shown using a simple model (Figure 1.12).

Note that the term frequency refers to the number of vibrations per unit of time, designated by the Greek letter \( \nu \) (nu) and generally specified in units of sec\(^{-1}\) or Hertz (Hz). Amplitude is defined by the interatomic distance covered at the extremes of the vibrating dipole and is dependent upon the amount of energy absorbed by the infrared active bond. When incoming photons from a spectrophotometer source lamp (after they have passed through the monochromator or interferometer) strike different molecules in a sample, two direct results may occur: (1) the disturbing energy does not match the natural vibrational frequency of the molecule; or (2) the disturbing frequency

![Figure 1.12](image-url)
Introduction to Near-Infrared Spectra

does match the vibrational frequency of the molecule. When there is a match between the disturbing frequency of the illumination energy and the natural vibrational frequency of a molecule in the sample, the molecule absorbs this energy, which in turn increases the vibrational amplitude of the absorbing dipoles. However, regardless of the increase in amplitude, the frequency of the absorbing vibration remains constant.

Another name for the dipole model from Figure 1.12 is an ideal harmonic oscillator. The frequency at which the dipole (or ideal harmonic oscillator) vibrates (stretches or bends) is dependent upon the bond strength and the masses of the atoms bonded together. When the harmonic oscillator (HO) vibrates, the vibrational energy is continuously changing from kinetic to potential and back again. The total energy in the bond is proportional to the frequency of the vibration. The use of Hooke’s law (in our case referring to the elasticity properties of the HO) is applied to illustrate the properties of the two atoms with a well-behaved spring-like bond between them. The natural frequency of vibration for a bond (or any two masses connected by a spring) is given by the well-known relationship

\[ v = \frac{1}{2\pi} \sqrt{\frac{K}{m_1 + m_2}} \]  

(1.7)

where K is a force constant that varies from one bond to another; \( m_1 \) = the mass of atom 1; and \( m_2 \) = the mass of atom 2. Note that as a first approximation, the force constant (K) for single bonds is 1/2 times that of a double bond and 1/3 that of a triple bond. Also note that as the mass of the atoms increases, the frequency of the vibration decreases.

Group theory can be used to represent the associations or bonds between the atoms of molecules into one-dimensional simple springs or simple harmonic oscillators. Normal mode theory, using the simple harmonic oscillator model, is able to predict with relative accuracy the energy or frequency of fundamental absorption bands, such as symmetric and asymmetric stretching, scissoring, bending, and wagging. However, for overtone band positions, normal mode theory does not predict band positions because bonds are not true harmonic oscillators. The effects of quantum mechanics on a simple HO indicate that we cannot treat the bond between two atoms quite as simply as two masses connected by a spring. This is no surprise because quantum mechanical evidence has shown that vibrational energy between atoms in a molecule is quantized into discrete energy levels. When the conditions are right, vibrational energy in a molecule “jumps” from one energy level to another. The discrete vibrational energy levels for any molecule \( E_{\text{VIB}} \) are given by

\[ E_{\text{VIB}} = h\nu \left( v + \frac{1}{2} \right) \]  

(1.8)

where \( h \) = Planck’s constant; \( \nu \) (Greek \( \nu \)) = vibrational frequency of the bond; and \( v \) = the vibrational quantum number (which can only have the integer values of 0, 1, 2, 3, and so on).

1.18 THE ANHARMONIC OSCILLATOR

The concept of an anharmonic oscillator allows for more realistic calculations of the positions of the allowed overtone transitions. The energy levels of these overtones are not found to be the product of the exact integer multiplied by the fundamental frequency. In fact, the following
expression defines the relationships between wavenumber (for a given bond) and the vibrational energy of that bond using local mode or anharmonicity theory. The relationship is calculated from the Schrödinger equation to yield

$$\tilde{\nu} = \left(\frac{E_{\text{vib}}}{hc}\right) = \tilde{\nu}_i \nu - x_i (\nu + \nu^2)$$  \hspace{1cm} (1.9)

where $\nu = \text{an integer number, i.e., 0, 1, 2, 3, …, n}$, and $x_i \tilde{\nu}_i$ = the unique anharmonicity constant for each bond.

Calculations of band positions using Equation 1.18 will more closely approximate observed band positions than those calculated from the ideal harmonic oscillator expression found in Equation 1.16. For a rule of thumb, the first overtone ($2\nu$) for a fundamental can be calculated as $1\%$ shift due to anharmonicity, or $x = (0.01)$. Thus, the expression using wavenumbers is

$$\tilde{\nu} = \tilde{\nu}_i \nu - \tilde{\nu}_i (0.01) \cdot (\nu + \nu^2)$$  \hspace{1cm} (1.10)

To illustrate the occurrence of free O–H first overtone absorption using a fundamental absorption occurring at approximately $3625 \text{ cm}^{-1}$, the first overtone (in wavenumbers) of free O–H stretching should occur at

$$\tilde{\nu} = (3625 \cdot 2) - 3625 (0.01) \cdot (2 + 2^2) = 7033 \text{ cm}^{-1} \text{ or } 1422 \text{ nm}$$  \hspace{1cm} (1.11)

Thus, one would expect the first overtone to occur somewhere near $7033 \text{ cm}^{-1}$ or $1422 \text{ nm}$ using a simple harmonic oscillator model (to convert to wavelength, use $10^7 \div \nu$ [in cm$^{-1}$]). Calculations for wavenumber positions for the first overtone ($2\nu$), second overtone ($3\nu$), and third overtone ($4\nu$) can be estimated with the assumption of a $1–5\%$ frequency shift due to anharmonicity.

Molecules that absorb NIR energy vibrate primarily in two fundamental modes: (1) stretching and (2) bending. Stretching is defined as a continuous change in the interatomic distance along the axis between two atoms, and bending is defined as a change in the bond angle between two atoms. Figure 1.13 illustrates the often repeated stretching and bending interactions defining infrared active species within infrared active molecules.

Note that near-infrared (12,821–4000 cm$^{-1}$, 780–2500 nm) spectral features arise from the molecular absorptions of the overtones and combination bands that originate from fundamental vibrational bands generally found in the mid-infrared region. For fundamental vibrations, there exists a series of overtones with decreasing intensity as the transition number (overtone) increases. Combination bands arise as the summation of fundamental bands, their intensity decreasing with an increase in the summation frequency. Most near-infrared absorptions result from the harmonics and overtones of X–H fundamental stretching and bending vibrational modes. Other functional groups relative to near-infrared spectroscopy can include hydrogen bonding, carbonyl carbon to oxygen stretch, carbon to nitrogen stretch, carbon to carbon stretch, and metal halides.

Molecular vibrations in the near-infrared regions consist of stretching and bending combination and overtone bands. Stretching vibrations occur at higher frequencies (lower wavelengths) than bending vibrations. Stretching vibrations are either symmetric or asymmetric; bending vibrations are either in-plane or out-of-plane. In-plane bending consists of scissoring and rocking; out-of-plane bending consists of wagging and twisting. From the highest frequency to lowest, the vibrational modes occur as stretching, in-plane bending (scissoring), out-of-plane bending (wagging), twisting, and rocking. The most-often observed bands in the near-infrared
include the combination bands and first, second, or third overtones of O–H, N–H, and C–H fundamentals.

Variations in hydrogen bonding manifest themselves as changes in the force constants of the X–H bonds. Generally, bands will shift in frequency and broaden due to the formation of hydrogen bonding. Because combination bands result from the summation of two or more fundamental vibrations, and overtones occur as the result of the multiples of fundamental vibrations, frequency shifts related to hydrogen bonding have a greater relative effect on combination and overtone bands than on their corresponding fundamentals. This feature of the near-infrared region alerts one to the importance of the relative hydrogen bonding effects brought about by solvent and temperature variations.

Precise band assignments are difficult in the near-infrared region because a single band may be attributable to several possible combinations of fundamental and overtone vibrations, all severely overlapped. The influence of hydrogen bonding results in band shifts to lower frequencies (higher wavelengths); a decrease in hydrogen bonding due to dilution and higher temperatures results in band shifts to higher frequencies (lower wavelengths). Band shifts of the magnitude of 10–100 cm\(^{-1}\), corresponding to a few to 50 nm, may be observed. The substantial effect of hydrogen bonding should be kept in mind when composing calibration sample sets and experimental designs for near-infrared experiments.

Near-infrared spectra contain information relating to differences in bond strengths, chemical species, electronegativity, and hydrogen bonding. For solid samples, information with respect to scattering, diffuse reflection, specular reflection, surface gloss, refractive index, and polarization of reflected light are all superimposed on the near-infrared vibrational information. Aspects related to hydrogen bonding and hydronium ion concentration are included within the spectra.

Light can interact with the sample as reflection, refraction, absorption, scattering, diffraction, and transmission. Signal losses from the sample can occur as specular reflection, internal scattering, refraction, complete absorption, transmission loss during reflectance measurements, and trapping losses. Spectral artifacts can also arise as offset or multiplicative errors due to coloration of the sample, variable particle sizes and resultant variability in apparent pathlength, refractive index
changes in clear liquids relative to temperature changes, and pathlength differences due to tempera-
ture-induced density changes.

During measurement of a sample, the light energy entering the sample will be attenuated to some
extent; the light entering the sample is able to interact with the sample, emerging as attenuated transmitted
or reflected light. The frequency and quantity of light absorbed yields information regarding both the
physical and compositional information of the sample. For reflection spectra, the diffuse and specular
energy fractions are superimposed. The intensity of reflected energy is a function of multiple factors,
including the angles of incidence and observation, the sample packing density, crystalline structure,
refractive index, particle size and distribution, and absorptive and scattering qualities.

The types of vibrations found in near-infrared and infrared spectroscopy are designated by \( \nu \)
(Greek letter nu) with a subscript designating whether the vibration is symmetric or asymmetric
and bending by \( \delta \). Combination bands resulting from the sum of stretching and bending modes are
designated as \( \nu + \delta \); harmonics are designated as \( k\nu \) where \( k \) is an integer number as 2 (first
overtone), 3 (second overtone), ..., \( k \) (\( k-1 \) overtone), and \( \nu \) is the frequency of the fundamental
stretch vibration for a specific functionality.

1.19 ILLUSTRATION OF THE SIMPLE HARMONIC OSCILLATOR
OR NORMAL MODE

The classical harmonic oscillator model or normal mode is often illustrated using a potential energy
curve (Figure 1.14). The larger the mass, the lower the frequency of the molecular vibration, yet the
potential energy curve does not change. The relationship for a simple diatomic molecule model is

\[
Frequency = \nu(nu) = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (1.12)
\]

where \( k \) is the force constant for the bond holding the two atoms together, and \( \mu \) is the reduced
mass from the individual atoms.

For any bond, there is a limit to the amplitude of motion away from and toward the opposing
atom (\( X_{\text{max}} \) and \( X_{\text{min}} \), respectively); the potential energy increases at either extreme, i.e., either the
minimum or maximum distance between atoms. The total potential energy (\( E_{\tau} \)) for a bond following
the harmonic oscillator model is given by \( E_{\tau} = \frac{1}{2}k \cdot x^2 \), where \( k \) is the force constant for the bond
holding the two atoms together, and \( x \) is the change in displacement from the center of equilibrium.
For any specific bond, there is a limit to the total energy and maximum displacement of the atoms
(or dipoles). Quantum mechanical theory is used to more closely describe the behavior of these
atoms connected by bonds with varying force constants. Using quantum theory, it is possible to
describe a mathematical relationship for the behavior of two oscillating atoms as following not a
continuous change in potential energy states for the vibrating system but actually a set of discrete
energy levels \( E_n \) given by \( E_n = (n+\frac{1}{2})\hbar\nu \), where \( n \) is the oscillating dipole quantum number for
discrete potential energy levels, i.e., 0, 1, 2, 3, ..., \( n \). The potential energy curve better describing
the behavior of oscillating dipoles is given in Figure 1.14.

1.20 THE SELECTION RULE

The selection rule states that, in the quantum mechanical model, a molecule may only absorb (or emit)
the light of an energy equal to the spacing between two levels. For the harmonic oscillator (dipole
involving two atoms), the transitions can only occur from one level to the next higher (or lower) level.

The infrared spectrum for any molecule will exhibit a band corresponding to the frequency of the
energy at which light can absorb, namely, \( E_0 \), \( E_1 \), \( E_3 \), and so on. Figure 1.14 illustrates the discrete
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1.21 ILLUSTRATION OF THE ANHARMONIC OSCILLATOR

The model of the anharmonic oscillator or local mode approximation more closely follows the actual condition for molecular absorption than that of the harmonic oscillator. Figure 1.15 illustrates the differences between the ideal harmonic oscillator case that has been discussed in detail for this chapter vs. the anharmonic oscillator model (better representing the actual condition of molecules). Unlike the ideal model illustrated by the harmonic oscillator expression, the anharmonic oscillator involves considerations such that, when two atoms are in close proximity (minimum distance), they repel each other; when two atoms are separated by too large a distance, the bond breaks. The anharmonic oscillator potential energy curve is most useful to predict behavior of real molecules.

1.22 INTERPRETIVE NEAR-INFRARED SPECTROSCOPY

The energy absorbed by a matrix consisting of organic compounds depends upon the chemical composition of the matrix, defined by the species (or type) of molecule present, the concentration of these individual species, and the interactions between the molecules in the matrix. In order for NIR (or any other vibrational spectroscopic measurement technique) to be valid, one must be absolutely assured that different types of molecules absorb at unique frequencies. Due to the broadband nature of NIR spectra consisting of overlapping combination and overtone bands, the individual species are not well resolved as they are in the mid-infrared region. In addition, many compounds absorb NIR energy throughout the entire wavelength region, making it difficult, if not...
impossible, to clearly resolve a usable baseline for simple peak-height or peak-area quantitative methods. This brings one to the same conclusion drawn by early investigators that the NIR region is not especially useful as a quantitative measurement technique. At the very least, novel techniques for spectral manipulation were required to “interpret” the poorly resolved bands and “compensate” for background interferences.

1.23 GROUP FREQUENCIES

Frequencies that are characteristics of groups of atoms (termed functional groups) are given common group names and can be assigned general near-infrared locations (in nanometers) for major groups associated with stretching vibrational bands. The locations of the fundamental frequencies, overtones, and combination bands are provided in this book. References 5 and 6 provide a rich source of information as to locations of fundamental frequencies for the major function groups (see Table 1.5 for examples) within the infrared and near-infrared regions.

1.24 COUPLING OF VIBRATIONS

Coupling indicates that the oscillators or molecular vibrations of two or more molecules are interactive, so that the original vibrational energy states (if the vibrations could occur independently of one another) result in split energy states due to the interaction of the vibrations. Coupling is divided into two basic orders: first and second (Fermi resonance). First-order coupling can be involved in several important infrared group frequencies. For example, CO₂ has two separate uncoupled oscillators of C=O, each occurring at approximately 5405 nm (ν at ~1850 cm⁻¹), 2756.6–2972.8 nm (2ν), 1855.7–2071.9 nm (3ν), and 1405.3–1621.5 nm (4ν). The interactive (coupled oscillators) energy states occur at 4257 nm (ν at 2349 cm⁻¹, asymmetric stretch), 2171.1–2341.4 nm (2ν), 1461.6–1631.9 nm (3ν), and 1106.8–1277.1 nm (4ν); and 7463 nm (ν at 1340 cm⁻¹, symmetric stretch), 3806.1–4104.7 nm (2ν), 2562.3–2860.8 nm (3ν), and 1940.4–2238.9 nm (4ν). First-order coupling involves multiple infrared group frequencies including:
The stretches for all cumulated double bonds, X=\(Y=Z\), e.g., C=C≡N
The stretches in \(XY_2\), including -CH_2- and \(H_2O\)
The stretches in \(XY_3\) groups, including -CH_3
The deformations of \(XY_3\) groups, including CH_2, CH_3, etc
The N–H in-plane bend of secondary amides, e.g., R–CO–NH–R

1.25 FERMI RESONANCE (OR SECOND-ORDER COUPLING)

Fermi resonance is the interaction or coupling of two vibrational energy states with the resultant separation of the states where one of them is an overtone or a sum tone. An overtone vibration occurs as the integer multiple of a fundamental vibration in frequency space (intensity falls off rapidly with the higher multiples):
The first overtone of a fundamental vibration (ν) is equal to $2 \times \nu$.
The second overtone of a fundamental vibration is equal to $3 \times \nu$.
The third overtone is equal to $4 \times \nu$.

**Note:** Overtones are a special case of sum tones where the frequencies are identical. A sum tone is the general case of an overtone where the frequencies are not equal and where a variety of vibrational energy states can occur.

A binary sum tone is equal to the sum of two fundamentals, e.g., $\nu_i + \nu_k$.
A ternary sum tone is equal to the sum of three fundamental vibrations, e.g.,

$$ \nu_i + \nu_k + \nu_m. $$

Other sum tones can occur such as the sum of an overtone and a fundamental vibration, e.g., $2\nu_i + \nu_k$.

Three requirements are stated for Fermi resonance:

1. The zero-order frequencies must be close together (typically within 30 cm$^{-1}$).
2. The fundamental and the overtone or sum tone must have the same symmetry.
3. There must be a mechanism for the interaction of the vibrations.

**Note:** (1) The vibrations cannot be separated (or localized) in distinctly different parts of the molecule. (2) The vibrations must be mechanically interactive in order that the interaction of one vibration affects another.

The results of Fermi resonance are important for infrared and near-infrared spectroscopy. Fermi resonance causes the following effects on spectral bands:

- The resultant bands are moved in position from their expected frequencies.
- Overtone bands are more intense than expected.
- There may exist doublet bands where only singlets were expected.
- Solvent changes can bring about slight shifts in frequency location of a band, and intensities can be greatly changed.

### 1.26 TOOLS AND TECHNIQUES FOR ASSIGNING BAND LOCATIONS

There are many current techniques used for assisting in near-infrared band assignments, including Darling–Dennison$^9$ resonance, deuteration, polarization, and two-dimensional (2-D) correlation spectroscopy. The scope of this book is practical rather than theoretical, and so the techniques are mentioned here for further investigation by the reader.

For some molecules, for example H$_2$O, the near-resonant frequencies of the symmetric (s) and asymmetric (a) stretches interact in such a way that the normal stretching modes in the molecule couple. Addition of the Darling–Dennison coupling in a molecule gives a band that is no longer separable into the two s and a modes. The Darling–Dennison coupling is for two modes s and a, which have approximately the same frequency, which is often called a 1:1 resonance coupling.

Heavy hydrogen or deuterium is used to deuterate compounds and correlate the changes in their near-infrared spectral band positions, intensities, and widths for both the deuterated (deuterium-labeled) and undeuterated (unlabeled) molecules. This experiment provides information for the
identification of the vibrational modes of the deuterated molecule based on the known or accepted assignments of the nondeuterated molecular forms.

Polarization and dichroism methods, such as variable circular dichroism (VCD) and magnetic circular dichroism (MCD), are used to determine band assignments in complex molecules. By using various models, polarization features can be correlated with the observed positions of bands in the near-infrared spectra. Absorption bands are assigned to short-axis polarized Q transitions measured using such techniques.

Two-dimensional correlation spectroscopy is used for detailed band assignment work. The technique allows spectral information to be analyzed that is much richer in information content than one-dimensional data. Cross-correlation analysis methods are applied to spectral combinations of NIR with NIR, or NIR and mid-infrared, allowing band assignments to be more easily accomplished. An excellent review paper describing the mathematics used in 2-D correlation spectroscopy along with several examples of generalized 2-D NIR and 2-D NIR-mid-infrared (MIR) heterospectral correlation analysis are introduced with 42 references by Ozaki and Wang.

REFERENCES

2 Alkanes and Cycloalkanes

2.1 C-H FUNCTIONAL GROUPS

The fact that aliphatic hydrocarbons had an absorption band at 1.7 \( \mu \)m was known as early as 1881.\(^1\) The assignment of this absorption as a first overtone of a C–H stretch vibration was perhaps first recognized by Joseph Ellis, although he initially felt that the 1.7-\( \mu \)m peak was part of a harmonic series that began with the 6.9-\( \mu \)m CH bending mode.\(^2\) Nevertheless, the assignment of the first overtone of carbon–hydrogen stretching vibrations was made very early in the history of near-infrared (IR) spectroscopy.

Aliphatic and aromatic C–H-stretching first overtones are rich in information content, having much the same information as the fundamental vibrations. In addition, the combinations of these stretches with other vibrational modes provide much of the spectral structure of the near-infrared region.

As a general assignment, the first overtones of C–H stretching occur between 5555 and 5882 cm\(^{-1}\) (1700–1800 nm), the second overtones between 8264 and 8696 cm\(^{-1}\) (1150–1210 nm), and the third overtones between 11,364 and 10,929 cm\(^{-1}\) (880–915 nm). The most important combination regions occur between about 6666 and 7690 cm\(^{-1}\) (1300–1500 nm) and 4545 and 4500 cm\(^{-1}\) (2200–2500 nm).

2.2 METHYL GROUPS, CH\(_3\)

Figure 2.1 shows an example with some general band assignments of the methyl C–H spectral regions for iso-octane (2,2,4-trimethyl pentane), a molecule that has mostly methyl groups.

2.2.1 FIRST OVERTONE REGION

As seen in Figure 2.2, a homologous series of alkanes has four main peaks in the first overtone region. In the mid-infrared fundamental region, these peaks represent the methyl asymmetric, methylene asymmetric, methyl symmetric, and methylene symmetric vibrations in the order from the highest to the lowest wavenumber. In the near-infrared, however, these peaks do not fall in this sequence, and their actual assignments are more complex. As shown in Figure 2.2, the two lower wavelength (higher wavenumber) peaks decrease as the chain length increases, clearly indicating that these two belong to the methyl group. These peaks have been referred to as the first overtones of the asymmetric and symmetric stretch vibrations, but this may be an oversimplification.

As described by Tosi and Pinto,\(^3\) who examined 50 linear and branched hydrocarbons, there are five primary bands in the first overtone region. The first appears at 5905 ± 4 cm\(^{-1}\) in all of the hydrocarbons and can be attributed to the methyl group. It is probably the first overtone of the asymmetric stretch of the methyl group. The position of the second peak decreases in wavenumber with an increase in chain length and follows the formula 5853 + 49F–CH\(_3\), where F–CH\(_3\) is the mole fraction of methyl groups in a given hydrocarbon. For hexane, for example, this peak would be estimated to be at 5876 cm\(^{-1}\). As seen in Figure 2.2, the methyl peaks of hexane are at 5907 and 5870 cm\(^{-1}\). The second peak appears to be initially stronger but becomes less distinct when the chain length is increased as it becomes affected by the neighboring methylene peak.
Within the classes of hydrocarbon compounds (linear, singly branched, doubly branched), good correlations between the peak intensities and the percent of the functional group can be obtained. In general, the absorptivity of terminal methyls is higher than that of internal or branched methyls.

As in the mid-infrared, the position of the C–H stretch vibrations can be affected by adjacent atoms. Table 2.1 lists some examples. Figure 2.3 illustrates the shift of the two methyl “overtone” peaks with the influence from the carbonyl group.

In addition to the two methyl peaks near 5790 and 5735 cm$^{-1}$, the methyl group in aromatic compounds has a band near 5660 cm$^{-1}$, which has been found useful for quantitative analysis. Luty and Rohleder$^4$ assigned this peak to be due to $\nu_s + 2\delta$. They also suggest that a peak at 4080 cm$^{-1}$ is due to $3\delta$, the second overtone of a symmetric bending vibration of the CH$_3$ group. This peak is well isolated in compounds having multiple methyl groups such as penta and hexa-methyl benzene.
Alkanes and Cycloalkanes

**FIGURE 2.2** First overtones of methyl and methylene C–H stretching; solid line is hexane, small dash heptane, dots nonane, long dash dodecane, and dot-dash hexadecane. (From Weyer, L.G. and Lo, S.–C., in *Handbook of Vibrational Spectroscopy*, Chalmers, J.C. and Griffiths, P.R., John Wiley & Sons, 2002. With permission.)

**TABLE 2.1**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Peak Positions (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliphatic, terminal R–CH₃</td>
<td>5905; 5876</td>
</tr>
<tr>
<td>Aliphatic, branched</td>
<td></td>
</tr>
<tr>
<td>CH₃</td>
<td>5905; 5872</td>
</tr>
<tr>
<td>–R–CH–R–</td>
<td></td>
</tr>
<tr>
<td>Aromatic, Ar</td>
<td>5790; 5735; plus 5650</td>
</tr>
<tr>
<td>Carboxyl</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>5960; 5898</td>
</tr>
<tr>
<td>–C–CH₃</td>
<td></td>
</tr>
<tr>
<td>Carboxyl, one carbon</td>
<td>5946; 5908</td>
</tr>
<tr>
<td>removed</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td></td>
</tr>
<tr>
<td>–C–CH₂CH₃</td>
<td></td>
</tr>
<tr>
<td>Hydroxyl</td>
<td>5880; 5773</td>
</tr>
<tr>
<td>Ether</td>
<td>5880; 5770</td>
</tr>
<tr>
<td>Amine</td>
<td>R–C–NH₂</td>
</tr>
<tr>
<td>Halogen</td>
<td></td>
</tr>
<tr>
<td>CH₃Cl</td>
<td>6000/6040 doublet, 5882 — gas</td>
</tr>
<tr>
<td>CH₃Br</td>
<td>6025/6060 doublet, 5900 — gas</td>
</tr>
<tr>
<td>CH₃I</td>
<td>6020; 5902; 5845</td>
</tr>
<tr>
<td>Nitro</td>
<td>6045; 5874</td>
</tr>
</tbody>
</table>
2.2.2 Higher-Order Overtones

As seen in Figure 2.1, the second, third, and fourth overtone regions (3ν, 4ν, and 5ν) have only one strong band. This was thought to be most likely due to the asymmetrical vibrations, as the symmetrical bands became relatively weaker in higher overtones. An alternate theory for this phenomenon is that local mode effects at the higher overtones combine to create only one general absorption peak. The second overtone is generally considered intermediate between the normal mode and local mode, whereas the higher-order overtones are only local mode.

The second overtone region (1150–1210 nm or 8264–8696 cm⁻¹) has also been used for quantitative measurements, in particular to measure methyl, methylene, methine, and aromatic contributions. The methyl groups of long-chain paraffinic hydrocarbons appear between 8365 and 8375 cm⁻¹ (1194–1195 nm). In pentane and hexane, the methyl group absorbs at 8396 cm⁻¹ (1191 nm), in heptane it absorbs at 8388 cm⁻¹ (1192 nm), and in decane it is at 8378 cm⁻¹ (1194 nm). See Figure 2.4.

The third overtone vibration of the methyl group appears at 10,953 in hexane. The methyl third overtone in some additional molecules is listed in Table 2.2. Wheeler assigns the fourth overtone’s position to be at about 13,400 cm⁻¹ (746 nm). Fang and Swofford list the fifth overtone for a linear alkane methyl group C–H stretch to be at 15,690 cm⁻¹ (637 nm), and the sixth at about 17,890 cm⁻¹ (560 nm).

2.2.3 Combination Bands

The first “combination” region near 4500–4545 cm⁻¹ (2200–2500 nm) is rich in information but complex, as it includes combinations of C–H stretching with various bending and stretching

![Absorbance/Wavenumber (cm⁻¹)](image-url)
vibrations from the mid-infrared “fingerprint” region. In addition, overtones of bending modes alone may be present.

For the methyl functional group, there is a strong peak near 4395 cm$^{-1}$ (2275 nm), as seen in Figure 2.5. This is probably a $\nu + \delta$ combination. There is also said to be a $3\delta$ peak of the symmetric methyl bending “umbrella” vibration near 4100 cm$^{-1}$ (2410–2460 nm).11,12 A $3\delta$ overtone of the asymmetric bending mode is expected to be at 4400 cm$^{-1}$ (2270 nm). A third overtone of the symmetric bending vibration, $4\delta$, is cited at about 5520 cm$^{-1}$ (1812 nm), whereas a third overtone of the asymmetric bending vibration is suggested to be at 5814 cm$^{-1}$ (1720 nm).

**FIGURE 2.4** The second overtone region, illustrating the separation of methyl and methylene contributions; the figure shows hexane (dotted curve), octane (dashed), and octadecane (solid).

**TABLE 2.2**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Peak Position (cm$^{-1}$)</th>
<th>Peak Position (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Bromoalkane</td>
<td>10,953</td>
<td>912</td>
</tr>
<tr>
<td>1-Heptene</td>
<td>10,953</td>
<td>912</td>
</tr>
<tr>
<td>$n$-Hexane</td>
<td>10,953</td>
<td>912</td>
</tr>
<tr>
<td>1-Amino hexane</td>
<td>10,941</td>
<td>914</td>
</tr>
<tr>
<td>2-Amino propane</td>
<td>10,977</td>
<td>911</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>11,052</td>
<td>905</td>
</tr>
<tr>
<td>3-chloro-2-methyl-1-propane</td>
<td>10,965</td>
<td>912</td>
</tr>
<tr>
<td>1-Octanol</td>
<td>10,953</td>
<td>912</td>
</tr>
<tr>
<td>Toluene</td>
<td>10,977</td>
<td>911</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>10,953</td>
<td>912</td>
</tr>
</tbody>
</table>
In the 7100-cm\(^{-1}\) (1400-nm) region of second combination bands, the double peak near 7355 cm\(^{-1}\) (1360 nm) and 7263 cm\(^{-1}\) (1377 nm) is suggested to be a combination of \(2\nu + \delta\).\(^{13}\) Also, in branched dimethyl alkanes, there is another, larger peak at 6938 cm\(^{-1}\) (1440 nm). This is shown in Figure 2.6.

**FIGURE 2.5** First combination region of 2,5-dimethyl hexane (solid line) and decane (dashed line).

**FIGURE 2.6** Illustration of branched hydrocarbon second combination band; 2,5-dimethyl hexane (solid line), hexane (dashed line), decane (dotted line).
2.3 METHYLENE GROUPS, CH₂

The general absorptions of methylene groups are illustrated in Figure 2.7, a spectrum of \( n \)-decane.

2.3.1 FIRST OVERTONE REGION — LINEAR MOLECULES

Methylene groups in linear, aliphatic molecules have two primary peaks at about 5800 cm\(^{-1}\) (1723 nm) and 5680 cm\(^{-1}\) (1762 nm) in the first overtone region. The 5800-cm\(^{-1}\) peak is generally thought to be a combination band,\(^{14}\) reported as \( \nu_a + \nu_s \).\(^{15}\) The 5680-cm\(^{-1}\) peak is considered to be a pure first overtone of the asymmetric stretch (Bubeck) or the symmetric stretch (Ricard-Lespade, Durbetaki). For solids, Bubeck lists both the asymmetric and symmetric stretches.

FIGURE 2.7 Illustration of Aliphatic C–H (as predominantly methylene C–H structure) from \( n \)-decane. The top spectrum (from left to right) shows the fourth overtone (5\( \nu \)), the third overtone (4\( \nu \)), and combination bands. The center spectrum illustrates the second overtone (3\( \nu \)) and combination bands. The bottom spectrum presents the first overtone (2\( \nu \)) and combination bands, and a portion of the fundamental. (From Workman, J., *Appl. Spectrosc. Revs.*, 31(3) 277, 1996. With permission.)
The 5800-cm\(^{-1}\) peak is usually the strongest peak in the first overtone region of a series of linear hydrocarbons. Tosi and Pinto provide a formula for locating this peak for a series of linear hydrocarbons: \(5856 - 85 \times \text{weight-fraction of CH}_2\), or about 5800 cm\(^{-1}\) for hexane. They also mention that this peak splits into two closely spaced peaks possibly due to the influence of adjacent methyl groups. The absorptivity of this combined peak does not regularly increase with chain length, probably because it has contributions from two sources.

The weaker methylene peak in the first overtone region was said to be at 5671 ± 3 cm\(^{-1}\) for linear hydrocarbons. This peak was thought to have contributions from both methyl and methylene groups (Tosi and Pinto), although others have assigned a 5680-cm\(^{-1}\) band to be both the first overtone of the methylene symmetric stretch and of the asymmetric stretch shifted by Fermi resonance (Ricard-Lespade et al.). More recently, Parker et al. have discussed the origins of this peak in terms of local mode theory.

In the second overtones, which are also shown in Figure 2.6, only one methyl and one methylene peak are normally observed at 8389 cm\(^{-1}\) (1192 nm) and 8264 cm\(^{-1}\) (1210 nm), although weaker peaks can be seen at 8673 cm\(^{-1}\) (1153 nm) and 8503 cm\(^{-1}\) (1176 nm) with higher resolution. In higher alkanes above dodecane, the methyl group becomes a shoulder in the methylene peak.\(^{16}\)

### 2.3.2 Higher-Order Overtones — Linear Molecules

The second overtone of the methylene C–H stretch absorption occurs at 8284 cm\(^{-1}\) (1207 nm) in pentane, 8271 cm\(^{-1}\) (1209 nm) in hexane, 8256 cm\(^{-1}\) (1211 nm) in heptane, and 8247 cm\(^{-1}\) (1212 nm) in decane. The third overtone is at 10,776 cm\(^{-1}\) (928 nm) in hexane. The peak positions of some additional compounds are provided in Table 2.3 from Salzer et al. The fourth overtone is at about 13,100 cm\(^{-1}\) (762 nm). Fang and Swofford also list the fifth overtone for a linear alkane methylene group C–H stretch to be at 15,400 cm\(^{-1}\) (649 nm), and the sixth at about 17,535 cm\(^{-1}\) (570 nm).\(^{17}\)

### 2.3.3 Combination Bands, Linear Molecules

The two largest peaks in the first combination region seen in Figure 2.7 are due to the asymmetric and symmetric methylene stretching and bending combinations.\(^{18}\) The asymmetric combination is at 4336 cm\(^{-1}\) in butane, 4334 in pentane, and 4332 in heptane, whereas the symmetric one is at 4257 in butane, 4262 in pentane, and 4259 in heptane, according to Ricard-Lespade et al.

In an examination of the spectrum of methylene chloride as interpreted by Kaye,\(^{19}\) the methylene combination peaks at 3945, 4196, 4253, and 4453 cm\(^{-1}\) in CH\(_2\)Cl\(_2\) are explained as \(\nu + \delta\) combinations as listed in Table 2.4. The analogous bands in a normal hydrocarbon would be at about 4068, 4168, 4261, and 4333 cm\(^{-1}\).
In the second combination region, shown in Figure 2.7, there is a doublet relating to the methylene group, the larger peak, at about 7186 cm\(^{-1}\) (1391 nm), and the smaller at about 7080 cm\(^{-1}\) (1412 nm). This doublet has been attributed to \(2\nu + \delta\).\(^{20}\) The \(2\nu\) term is neither asymmetric nor symmetric, as the vibrations are uncoupled at this point. Kaye called it \(\nu_a + \nu_s\). Also, \(\delta\) would include rocking, twisting, and/or bending vibrations. The two strongest bands are probably \(2\nu + \delta_b\) and \(2\nu + \delta_t\), based on Kaye’s description of the spectrum of methylene chloride.

There are also a number of weaker combination bands in the area between the first combination and the first overtones regions, 4500–5500 cm\(^{-1}\) or about 1800 to 2220 nm. These include \(\nu_a + 2\delta_r\), \(\nu_s + \delta_r + \delta_t\), \(\nu_s + 2\delta_t\), and \(\nu_a + \delta_r + \delta_t\).

### 2.3.4 First Overtones, Cyclic Molecules

The first overtone stretching vibrations of methylene groups of strained-ring cyclic compounds such as cyclopropane occur near 6135 cm\(^{-1}\) (1630 nm). The effects of various substituents on the ring have been studied by several authors. Gassman and Zalar\(^{21}\) list the band positions of 37 cyclopropane derivatives. Gassman\(^{22}\) also published a table of first overtone CH band positions of aliphatic nortricyclene derivatives. These overtones were at slightly lower wavenumber maxima than the cyclopropanes — about 6024 cm\(^{-1}\) (1660 nm).

The C–H stretch first overtone region of cyclohexane has two strong peaks at 5697 cm\(^{-1}\) (1755 nm) and 5791 cm\(^{-1}\) (1727 nm). A number of smaller, additional peaks were also seen by curve resolution.\(^{23}\) The two strongest peaks are probably \(2\nu_a\) and \(2\nu_s\)\(^{24}\) with the intensity of the symmetric band being intensified by Darling–Dennison resonance.

Cyclopentane, cyclobutane, cyclopropane, and many other cyclic molecules have been studied. In the fundamental region, the frequency increases as the ring becomes more strained, and the first overtones reflect this trend. Cyclopentane’s two strongest first overtone peaks are at 5730 cm\(^{-1}\) (1745 nm) and 5834 cm\(^{-1}\) (1714 nm) for example, as compared to cyclohexane’s 5697 and 5791 cm\(^{-1}\).

Inductive effects on cyclopropane’s first overtone have been extensively documented.\(^{25,26}\) There is a shift from 6158 cm\(^{-1}\) (1624 nm) to 6060 cm\(^{-1}\) (1650 nm) in moving from strongly electron-withdrawing groups such as cyano to strongly electron-inducing groups such as methyls.

A terminal epoxy ring is one case in which methylene C–H groups are influenced by the strained structure and an oxygen atom. Such epoxides, such as epichlorohydrin and 1,2-diisobutylene oxide, have a sharp absorption band at about 6060 cm\(^{-1}\) (1650 nm) with a molar absorptivity of about 0.2 l/mol-cm.\(^{27}\)

### 2.3.5 Higher-Order Overtones, Cyclic Molecules

For cyclohexane, the second overtone of the C–H stretch is probably a combination of normal and local mode effects, with the two major bands being related to oscillators localized on the axial and equatorial C–H bonds.\(^{28}\) The larger peak, near 8290 cm\(^{-1}\) for cyclohexane, 8434 cm\(^{-1}\) for cyclopentane, and 9116 cm\(^{-1}\) (1097 nm)\(^{29}\) for cyclopropane, has been used for characterizing various cyclic structures from petroleum fractions.\(^{30}\)

---

**TABLE 2.4**

First Combination Bands of Methylene Groups in CH\(_2\)Cl\(_2\)

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Peak Observed (cm(^{-1}))</th>
<th>Peak Calculated</th>
<th>Summation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu_a + \delta_r)</td>
<td>3945</td>
<td>3951</td>
<td>3055 + 896</td>
</tr>
<tr>
<td>(\nu_a + \delta_t)</td>
<td>4196</td>
<td>4211</td>
<td>3055 + 1156</td>
</tr>
<tr>
<td>(\nu_s + \delta_r)</td>
<td>4253</td>
<td>4251</td>
<td>2987 + 1264</td>
</tr>
<tr>
<td>(\nu_s + \delta_t)</td>
<td>4453</td>
<td>4477</td>
<td>3055 + 1422</td>
</tr>
</tbody>
</table>

*Note:* “r” denotes a rocking vibration, “t” twisting, “w” wagging, and “b” bending.
Higher overtones of cyclopentane, cyclobutane, and cyclopropane have also been studied with regard to their information content on equatorial and axial conformations.\(^{31}\) It is generally acknowledged that these higher overtones are explained by local mode theory.

The second overtone of the C–H stretch connected to an epoxy ring has been used for quantitative work.\(^{32}\) The peak appears at 8620 cm\(^{-1}\) (1160 nm).

### 2.3.6 Combination Bands, Cyclic Molecules

The 4545-cm\(^{-1}\) (2220-nm) combination band of the cyclopropane group has been studied along with the first overtone, and has been found to also shift to higher frequencies with electron-withdrawing power.\(^{33,34}\) The assignment is probably a \(\nu + \delta\) combination.

Terminal epoxides have a similar combination band that has been used for quantitative analysis following the cure of epoxy resins.\(^{35}\) It appears at about 4525 cm\(^{-1}\) (2210 nm) and has an absorptivity of about 1.5 l/mol-cm.\(^{36}\)

### 2.4 Methine Groups

The absorption of the single methine proton in the presence of methyl and methylenes is generally too small to be observed and is little mentioned in the literature. In the mid-infrared, the fundamental peak is near 2900 cm\(^{-1}\), between the methyl and methylene doublets. This would suggest that its first overtone was also in the envelope of small peaks in the 5882–5555-cm\(^{-1}\) (1700–1800-nm) region.

Wheeler\(^{37}\) gives the second overtone of an aliphatic methine to be 8163 cm\(^{-1}\) (1225 nm), and a second combination band to be at 6944 cm\(^{-1}\) (1440 nm).

The isolated aliphatic C–H group has been studied in halogenated compounds.\(^{38}\) Table 2.5 lists the band assignments for chloroform and bromoform, expressed in terms of normal modes. The authors mention that some of these bands are split by the nondegeneracy of the deformation vibrations. These assignments are in agreement with those of Kaye.\(^{39}\)

Iwamoto et al.\(^{38}\) also discuss the effect of the isolation of the C–H group in the CHX\(_3\) and CHX\(_2\)-CX\(_2\)-CHX\(_2\) molecules, in comparison with the coupled modes of CHX\(_2\)-CHX\(_2\) molecules. In the latter case, additional peak splitting is observed.

In general, the spectral features of vibrations of haloalkanes are affected by the mass of the halogen atom and the force constant of the carbon–halogen bond. If a halogen is bound to the same carbon atom as the hydrogen, the neighboring C–H overtone bands are shifted to a lower wavelength and their intensities are intensified.\(^{40}\)

### 2.5 Model Compound Comparisons

Figures 2.8 through 2.12 illustrate the general C–H absorption spectra–structure correlation by using three model compounds: trimethylpentane, \(n\)-decane, and toluene. Note that there are 12 methyl C–H bonds and 6 methylene C–H bonds in trimethyl-pentane; and there are 6 methyl C–H bonds and 16 methylene C–H bonds in \(n\)-decane. In the toluene molecule, there are 3 methyl C–H bonds; 0 methylene C–H bonds; and 5 aromatic C–H bonds.
FIGURE 2.8 Specific illustration of the fourth overtone (5 ν) near-infrared C–H stretch as aromatic C–H, methyl C–H, and methylene C–H stretching band positions in nanometers (nm), with band positions labeled in wavenumbers (cm⁻¹). Within the same figure is shown the third overtone (4 ν) combination region. For the third overtone (4 ν) combination region, methyl stretching and methyl bending combination bands indicated between 800 and 820 nm (12,500 to 12,195 cm⁻¹) are observed. Also observed are methylene stretch and the bending combination bands between 830 and 840 nm (12,048 to 11,905 cm⁻¹).

FIGURE 2.9 Demonstration of the third overtone (4 ν) harmonic and the second overtone (3 ν) combination region, illustrating the relative intensities and band positions. The third overtone (4 ν) near-infrared C–H stretching aromatic, methyl, and methylene band positions are shown. A region of second overtone (3 ν) combination bands is also seen in this figure.
FIGURE 2.10 Illustration of the second overtone (3 \( \nu \)) spectral region. Also observed are the first overtone (2 \( \nu \)) stretching and bending combination bands for methyl and methylene as labeled in the figure.

FIGURE 2.11 A spectrum of the first overtone (2 \( \nu \)) spectral region. For these bands we are able to observe both asymmetric and symmetric C–H stretching bands, which were not visible in spectra from the second (3 \( \nu \)), third (4 \( \nu \)), or fourth (5 \( \nu \)) overtone C–H stretching band regions (Figure 2.8 to Figure 2.10). Within this spectral region one observes the aromatic C–H as a single band, but clearly observes the asymmetric methyl and symmetric methylene stretching as separate bands. We also see that two bands are present for the asymmetric and symmetric methylene stretching.
Alkanes and Cycloalkanes

REFERENCES


**FIGURE 2.12** A spectrum of the first combination region for the model compounds. From these spectra of the model compounds, one observes the complexity of the combination region starting from about 2100 nm (i.e., 4762 cm⁻¹) and extending to near 3000 nm (i.e., 3333 cm⁻¹). There has not been comprehensive assignment work done for each of these bands. A few assignments are labeled in the figure. For example, the asymmetric methylene C–H stretching plus C–H bending combination band is shown near 2308 nm (i.e., 4333 cm⁻¹). This figure also shows the symmetric methylene C–H stretching plus C–H bending combination band near 2347 to 2350 nm (i.e., 4261 to 4255 cm⁻¹). This spectral region is also the location for the second overtone (2ν) methyl bending band near 2476 nm (i.e., 4039 cm⁻¹). Additional discussion of this spectral region was presented earlier in this chapter.
20. Murray, I., op. cit.
30. Evans, A. et al., op. cit.
33. Weitkamp, H., op. cit.
Alkenes and Alkynes

3.1 LINEAR ALKENES, OVERTONES

The first overtone of the C–H stretch next to a double bond occurs at a higher wavenumber (lower wavelength) than saturated C–H stretch absorptions. This peak is strong and distinct in some structures, particularly the methylene group of terminal double. In most cases, however, it is weak and difficult to locate especially in the presence of methyl groups. The band position is near 6100–6200 cm$^{-1}$ (1640–1612 nm).

The C–H stretch first overtone of terminal methylene groups of vinyl and vinylidene structures is isolated enough that it can be used in traditional quantitative analysis. Figure 3.1 provides one example, and Table 3.1 provides some typical peak locations. Goddu provides tables of absorptivities for the first overtone absorption of the terminal methylene group in a variety of compounds and solvents. Molar absorptivities are about 0.2–0.5 l/mol-cm. Put another way, a 100-ppm amount of methylene gives an absorbance of 0.01 in a 10-cm cell. Analyses using this peak to measure the vinyl content of acrylate monomers, butadienes, and edible oils have been reported.

In studies of wavelength displacement of deuterium substitution, hexadeuteropropylene (CD$_3$CD=CD$_2$) gives an asymmetric stretching of the CD$_2$ at 4610 cm$^{-1}$ (2170 nm).

In acrylates, in addition to the first overtone near 6000 cm$^{-1}$ (1665 nm), there is a band at 6167 cm$^{-1}$ (1620 nm), with overtones at 9020 cm$^{-1}$ (1109 nm) and 11,800 cm$^{-1}$ (847 nm), used by Gerasimov and Snively to study diacrylate and dimethacrylate reactions. Although this is said to be a combination band, it is a combination of two C–H stretch vibrations, rather than a C–H with another type of vibration.

The C–H stretch first overtone of a cis double bond has also been found to be distinct. It appears near 5963 cm$^{-1}$ (1677 nm) and is isolated from the vinyl overtones. Figure 3.2 illustrates the features of cis C–H absorptions in comparison to a trans configuration.

The second overtone of the terminal methylene C–H stretch can also be used for quantitative analysis. It occurs at about 9260 cm$^{-1}$ (1080 nm). In 1-alkenes, it is 8897–8944 cm$^{-1}$ (1118–1124 nm), with a molar absorptivity of 0.004–0.018 l/mol-cm. The peak is at 9017 cm$^{-1}$ (1109 nm) in allyl stearate and a doublet at 8787–9009 cm$^{-1}$ (1110–1138 nm) in alkyl acrylates. The peak is at 9091 cm$^{-1}$ (1100 nm) in alkyl vinyl ethers and about 9059 cm$^{-1}$ (1104 nm) in vinyl esters.

The third overtone of terminal methylenes' C–H stretch is found at 11,390 cm$^{-1}$ (878 nm) in 1-alkenes. Its absorptivity is 0.002 l/mol-cm. The alkyl acrylate doublet occurs at 11,905 and 12,500 cm$^{-1}$ (800 and 840 nm). The peak is at 10,776–11,360 cm$^{-1}$ (880–928 nm) in alkyl vinyl ethers, and 10,788–10,929 cm$^{-1}$ (915–927 nm) in vinyl ethers and vinyl esters. The fourth through seventh overtones of terminal methylene C–H stretch peaks have been studied using photoacoustic spectroscopy. These were given as approximately 11,450, 14,090, 16,630, and 18,800 cm$^{-1}$, respectively (873, 710, 600, and 532 nm, respectively). In the spectrum of propylene, this peak is split into a doublet of two peaks that are cis and trans to the methyl group.

3.2 LINEAR ALKENES, COMBINATIONS/BENDING MODES

A distinctive set of bands in the combination region exists for vinyl double bonds. As seen in Figure 3.1, there are three peaks at about 4482 cm$^{-1}$ (2230 nm), near 4600 cm$^{-1}$ (2170 nm), and 4670–4780 cm$^{-1}$ (2090–2140 nm).
The vinyl group in polybutadienes has been studied more extensively than simple alkenes, and it has a similar spectrum with peaks at about 4484, 4597, and 4660 cm\(^{-1}\). Bands at 4717 and 4481 cm\(^{-1}\) in polybutadiene have been assigned as second overtones of the symmetric and asymmetric bending vibrations of the CH\(_2\) of the uncoupled vinyl group, as interpreted by a local mode model.\(^{12}\) There are no corresponding fundamental vibrations for these peaks at 1469 and 1572 cm\(^{-1}\) though;

![Absorbance/Wavenumber (cm\(^{-1}\))](image)

**FIGURE 3.1** Hexane (solid) and 1-hexene (dotted).

The vinyl group in polybutadienes has been studied more extensively than simple alkenes, and it has a similar spectrum with peaks at about 4484, 4597, and 4660 cm\(^{-1}\). Bands at 4717 and 4481 cm\(^{-1}\) in polybutadiene have been assigned as second overtones of the symmetric and asymmetric bending vibrations of the CH\(_2\) of the uncoupled vinyl group, as interpreted by a local mode model.\(^{12}\) There are no corresponding fundamental vibrations for these peaks at 1469 and 1572 cm\(^{-1}\) though;

**TABLE 3.1**

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>CH Peak in cm(^{-1})</th>
<th>CH Peak in nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl (hexene) CH(_2)=CH-</td>
<td>6120</td>
<td>1635</td>
</tr>
<tr>
<td>Vinylidene (3-chloro-2-methyl-1-propene) CH(_2)=C&lt;</td>
<td>6130</td>
<td>1631</td>
</tr>
<tr>
<td>Vinyl on N (1-ethenyl 2-pyrrolidinone)</td>
<td>6170</td>
<td>1621</td>
</tr>
<tr>
<td>Vinyl on O (1-ethenyoxybutane)</td>
<td>6200</td>
<td>1613</td>
</tr>
<tr>
<td>Vinyl and vinylidene (2-methyl-1,3-butadiene)</td>
<td>6130/6140</td>
<td>1631/1629</td>
</tr>
<tr>
<td>Acrylate R–O–C–CH=CH(_2)</td>
<td>6169(^{a})</td>
<td>1621(^{a})</td>
</tr>
<tr>
<td>Methyne (1-hexyne) CH≡</td>
<td>6536</td>
<td>1530</td>
</tr>
</tbody>
</table>

\(^{a}\) According to Gerasimov and Snavely,\(^{7}\) this peak is actually a combination of vibrations, one quantum of energy from each of the two C–H bonds of the vinyl group, and the actual first overtone is at 5998 cm\(^{-1}\) (1667 nm).
only the overtones are observed. The overtones at 2X and all other even multiples are not observable because they coincide with stronger C–H-stretching vibrations. The vinyl peak, at 4600 cm$^{-1}$, has also been attributed to a bending mode by Snively and Angevine, as has the 4717 cm$^{-1}$ peak. These vinyl bands have also been discussed by McManis and Gast.\cite{13}

The 4482-cm$^{-1}$/2230-nm peak has been used to quantify the vinyl group having an absorptivity of about 0.87 l/mol-cm. The peak shifts slightly in allyl esters and ethers and splits into two peaks when a carbonyl is present. The 4600-cm$^{-1}$/2170-nm peak was observed in all vinyl compounds except vinyl esters. Its absorptivity is about 0.2 l/mol-cm. The 4700-cm$^{-1}$/2100-nm peak has an absorptivity of about 0.45 l/mol-cm.

Higher-order overtones of the 4481- and 4717-cm$^{-1}$ peaks have also been noted at 7346 cm$^{-1}$ (1360 nm) and 7750 cm$^{-1}$ (1290 nm). The 4600-cm$^{-1}$ peak also shows a second member of a progression at 7508 cm$^{-1}$ (1332 nm). Its absorptivity has been reported to be about 0.01 l/g-cm.

As in the C–H stretch overtones, trans double bonds do not have distinctive absorptions in the combination region, but cis double bonds do. There is a strong cis peak near 4673 cm$^{-1}$ (2140 nm) that can be used for quantification, and a second peak near 4587 cm$^{-1}$ (2180 nm). These peaks are pointed out in Figure 3.2.

### 3.3 CYCLIC DOUBLE BONDS

When cyclohexene is compared to cyclohexane, the most readily apparent difference occurs at the combination band near 4670 cm$^{-1}$ (2140 nm), similar to the cis double bond in straight-chain alkenes. There are additional bands in the overtone area as well. A small doublet near 6050 cm$^{-1}$ (1650 nm) might also be attributed directly to the C–H stretch next to the double bond. See Figure 3.3.

Cyclopentene also has a distinct combination band near 4660 cm$^{-1}$ (2145 nm) and four peaks near 6000 cm$^{-1}$ (1667 nm) that are not present in cyclopentane. At 8777 cm$^{-1}$ (1140 nm) there is

![Figure 3.2](DK4715_C003.fm)
Practical Guide to Interpretive Near-Infrared Spectroscopy

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a single, very distinctive C–H second overtone due to the C–H of the double bond. Wong and associates have analyzed and discussed the fifth overtone spectra of cyclic alkenes.

The first overtone of the C–H stretch of the double bond in norbornenes was determined to be in the range of 5970–6080 cm\(^{-1}\) (1645–1675 nm). The attribution of this absorption band to the C–H groups next to the double bonds and not the bridgehead C–H was confirmed by examination of model compounds that lacked the vinyl C–Hs and retained the bridgehead C–H. The effect of a number of different substituents on the band position was also studied.

3.4 DIENES

Dienes are described by the following structure and comprise a set of molecules with somewhat unique properties.

\[
\begin{align*}
\text{C} & \equiv \text{C} \\
\text{C} & \equiv \text{C}
\end{align*}
\]

As in aromatic compounds, dienes demonstrate multiple bands associated with conjugated double-bond and C–H stretching. The mid-infrared spectra of conjugated polyynes exhibit a band in the 1000- to 900-cm\(^{-1}\) (10,000- to 11,111-nm) region, which does not have overtones or combination bands observed in the near-infrared. This band is indicative of cis and trans groups within the different polyynes. The near-infrared bands associated with νH–C=C are observed near 6110 cm\(^{-1}\) (1637 nm), 5960 cm\(^{-1}\) (1678 nm), 4710 cm\(^{-1}\) (2123 nm), 4595 cm\(^{-1}\) (2176 nm), and 4470 cm\(^{-1}\) (2237 nm) and are very similar to those shown for 1-hexene in Figure 3.1. The 3νC=C band is observed near 4950 cm\(^{-1}\) (2020 nm). Note that the Appendix material provides more examples of model spectra as well as tables showing precise band positions.

FIGURE 3.3 Cyclohexane (solid curve) and cyclohexene (dotted).
3.5 ALKYNES AND ALLENES

The C–H stretch of a proton next to a triple bond occurs near 6500 cm$^{-1}$ (1538 nm) and is very distinctive and isolated from other C–H absorption peaks. There is also a combination band at 3930 cm$^{-1}$ (2545 nm) that could be the sum of the C–H stretch and the C–H wag. These are shown in Figure 3.4. 2-Hexyne, which has no proton on its triple bond, is shown for comparison. A second overtone of the C–H stretch occurs at about 9600 cm$^{-1}$ (1042 nm).

Allene, H$_2$C=C=CH$_2$, is said to have its first C–H overtone at 6139 cm$^{-1}$ (1629 nm) and a combination band at 6031 cm$^{-1}$ (1658 nm). Second and third overtones have been reported at 8620 cm$^{-1}$ and 11,765 cm$^{-1}$, respectively (1160 and 850 nm, respectively). 18

REFERENCES

4 Aromatic Compounds

4.1 BENZENE

The near-infrared (IR) spectrum of benzene has been thoroughly described by Kaye and others. Benzene is such a highly symmetrical molecule that only a few of its vibrations are infrared active. However, the inactive modes participate in the overtones and combinations of the near-infrared. An explanation for the nomenclature of the fundamental vibrational modes used by Kaye is provided in Figure 4.1 from Avram and Mateescu. Only the vibrations labeled “IR” have fundamental IR bands. The band assignments for the first combination and first overtone regions are provided in Table 4.1, using the Herzberg nomenclature as described in Figure 4.1.

The first overtone doublet near 6000 cm\(^{-1}\) (1670 nm) is actually composed primarily of IR-inactive C–H-stretching vibrations. As described in Table 4.1 and Figure 4.1, both of the bands near 6000 cm\(^{-1}\) are composed of a Raman active vibration and a vibration that is neither IR nor Raman active. The benzene NIR spectrum is shown in Figure 4.2.

The second overtone peak at 8834 cm\(^{-1}\) (1132 nm) represents the second overtone of the IR-active C–H stretch (vibration 12 in Herzberg notation and Figure 4.1). A nearby peak at 8770 cm\(^{-1}\) (1140 nm) has been assigned as a combination of twice the C–H stretch plus either 14 and 19, or 8 and 9. A third overtone is at 11,442 cm\(^{-1}\) (874 nm) neat, and 11,364 cm\(^{-1}\) (880 nm) in carbon tetrachloride. The fourth overtone is at about 14,000 cm\(^{-1}\) (714 nm).

The strong peak at 4050 cm\(^{-1}\) (2469 nm) is therefore a combination of vibrations 14 and 15 of Figure 4.1, a C–H stretch and C–H bending as described in the figure. The series of absorptions near 4660 cm\(^{-1}\) (2146 nm) combine C–C stretching with C–H stretching. Combination peaks near 3640 cm\(^{-1}\) (2747 nm) are C–H stretching combined with C–C or C–H-wagging vibrations.

Deuterated benzene (C\(_6\)D\(_6\)) has bands at 1900, 1560, 1375, and 1010 nm, which correspond to the first, second, third, and fourth overtones of C-D stretching, respectively.

4.2 SUBSTITUTED AROMATICS — ALKYL

Substitution on the benzene ring reduces the symmetry of the molecule, potentially allowing for additional vibrational peaks. In the case of alkyl aromatics, there is also the addition of the alkyl absorptions. Figure 4.2 compares the near-infrared spectra of benzene and toluene. The primary differences appear to be the addition of the methyl combination bands near 4300 cm\(^{-1}\) (2300 nm) and the methyl first overtones near 5800 cm\(^{-1}\) (1750 nm). There is also a noticeable peak at 3836 cm\(^{-1}\) (2607 nm) that could be related to the sum of a C–H stretch and one of the ring-wagging vibrations involving a ring with five adjacent protons.

Alkyl groups on the benzene ring displace the CH overtone band to a higher wavenumber (longer wavelength) due to their electropositive nature. Also, as seen in Figure 4.4, the strong peak in the region of 4060 cm\(^{-1}\) (2460 nm) is a doublet in mono-, di-, and tri-substituted methylbenzenes. The lower wavenumber peak in this doublet has been attributed to the C–H stretch/CC bending mode described in the preceding text, whereas the peak near 4080 cm\(^{-1}\) (2452 nm) has been assigned as the second overtone of the symmetric methyl-bending vibration. A linear relationship was found between the number of methyl groups substituted on the benzene ring and the intensity of this characteristic absorption band. The 4080-cm\(^{-1}\) band gave a good measure for aromatic compounds with 1 to 4 methyl groups. In higher-substituted methyl-benzenes such as durene and pentamethylbenzene, the first overtone band at 5660 cm\(^{-1}\) (1767 nm) provides better predictions.
With regard to higher vibrational states, the second overtone of the aromatic C–H stretch in alkylated benzenes occurs at 8734 cm$^{-1}$ (1145 nm), whereas the alkyl C–H stretch occurs at 8389 cm$^{-1}$ (1192 nm). Approximately 5- to 10-nm shifts were observed to lower frequency (longer wavelength) as compared with benzene’s second CH overtone band.

4.3 SUBSTITUTED AROMATICS — NONALKYL

As shown in Figure 4.5, electronegative groups such as halogens or nitro groups produce shifts to higher wavenumber (lower wavelength), whereas electropositive substituents (alkyl groups) generate a displacement to lower wavenumber.

In an investigation of NIR absorptions using photoacoustic experiments, the tentative assignments of 11 substituted benzenes have been reported. These included three benzonitriles, five acetonitriles, and three benzylbromides. An example of a typical group of band assignments, for 2,2,4-trichloroacetophenone, given in this work is:

4057 cm$^{-1}$ (2465 nm)  sum of 2927 and 1070 cm$^{-1}$
4141 cm$^{-1}$ (2415 nm)  sum of 3100 and 1070 cm$^{-1}$
### TABLE 4.1
Benzene Band Assignments

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Vibrations</th>
<th>Calculated Wavenumber</th>
<th>Observed Wavenumber</th>
<th>Observed Wavelength (nm)</th>
</tr>
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<tr>
<td>18 + 5</td>
<td>CCδ+CHv</td>
<td>3666</td>
<td>3613 (3613)</td>
<td>2768</td>
</tr>
<tr>
<td>12 + 18</td>
<td>CHv+CCδ</td>
<td>3705</td>
<td>3640 (3643)</td>
<td>2747</td>
</tr>
<tr>
<td>8 + 5</td>
<td>CCν+CHv</td>
<td>3731</td>
<td>3693 (3697)</td>
<td>2708</td>
</tr>
<tr>
<td>4 + 1</td>
<td>CHν+CHv</td>
<td>3733</td>
<td>Masked</td>
<td></td>
</tr>
<tr>
<td>7 + 5</td>
<td>CCν+CHv</td>
<td>3763</td>
<td>3722 (3735)</td>
<td>2687</td>
</tr>
<tr>
<td>11 + 12</td>
<td>CCν+CHv</td>
<td>3948</td>
<td>3937 (3935)</td>
<td>2540</td>
</tr>
<tr>
<td>19 + 15</td>
<td>CCν+CHv</td>
<td>4017</td>
<td>3960 (3958)</td>
<td>2525</td>
</tr>
<tr>
<td>15 + 6</td>
<td>CHν+CCδ</td>
<td>4047</td>
<td>3980 (3986)</td>
<td>2513</td>
</tr>
<tr>
<td>14 + 15</td>
<td>CCδ+CHν</td>
<td>4084</td>
<td>4050 (4060)</td>
<td>2469</td>
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<td>4091</td>
<td>Shoulder</td>
<td></td>
</tr>
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<td>14 + 1</td>
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<td>4099</td>
<td>Shoulder</td>
<td></td>
</tr>
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<td>4155 (4175)</td>
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<tr>
<td>17 + 5</td>
<td>CCδ+CHν</td>
<td>4238</td>
<td>4190 (4198)</td>
<td>2387</td>
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<tr>
<td>12 + 17</td>
<td>CHν+CHδ</td>
<td>4277</td>
<td>4252 (4263)</td>
<td>2352</td>
</tr>
<tr>
<td>12 + 3</td>
<td>CHν+CHδ</td>
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<td>4360 (4379)</td>
<td>2294</td>
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<tr>
<td>13 + 15</td>
<td>CCν+CHv</td>
<td>4532</td>
<td>4532 (4549)</td>
<td>2206</td>
</tr>
<tr>
<td>13 + 1</td>
<td>CCν+CHv</td>
<td>4547</td>
<td>4570 (4584)</td>
<td>2188</td>
</tr>
<tr>
<td>16 + 5</td>
<td>CCν+CHv</td>
<td>4656</td>
<td>4615 (4625)</td>
<td>2167</td>
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<td>12 + 16</td>
<td>CHν+CCv</td>
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<td>4642 (4644)</td>
<td>2154</td>
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<tr>
<td>15 + 9</td>
<td>CHν+CCv</td>
<td>4695</td>
<td>4655 (4675)</td>
<td>2148</td>
</tr>
<tr>
<td>15 + 5</td>
<td>CHν+CHv</td>
<td>6107</td>
<td>5920 (5914)</td>
<td>1689</td>
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<td>12 + 1</td>
<td>CHν+CHv</td>
<td>6161</td>
<td>5985 (5988)</td>
<td>1671</td>
</tr>
</tbody>
</table>

*Note*: The wavenumbers in parentheses represent peak positions determined by the author in Reference 1.

4246 cm⁻¹ (2355 nm) sum of 3100 and 1162 cm⁻¹
4320 cm⁻¹ (2315 nm) sum of 2950 and 1406 cm⁻¹
4494 cm⁻¹ (2225 nm) sum of 2950 and 1479 cm⁻¹
4651 cm⁻¹ (2150 nm) sum of 3100 and 1590 cm⁻¹
4938 cm⁻¹ (2025 nm) sum of 2998/2950 and 2 × 991 cm⁻¹
5141 cm⁻¹ (1945 nm) 3 × 1716 cm⁻¹
5291 cm⁻¹ (1890 nm) sum of 3100 and 2 × 1070 cm⁻¹
5540 cm⁻¹ (1805 nm) sum of 2950 and 2 × 1282 cm⁻¹
5731 cm⁻¹ (1745 nm) 2 × 2858 cm⁻¹
5935 cm⁻¹ (1685 nm) 2 × 2950 cm⁻¹
6173 cm⁻¹ (1620 nm) 2 × 3100 cm⁻¹
6431 cm⁻¹ (1555 nm) sum of 2998 and 2 × 1708 cm⁻¹
6667 cm⁻¹ (1500 nm) 2 × 2950 plus 727 cm⁻¹
6897 cm⁻¹ (1450 nm) 2 × 2950 plus 991 cm⁻¹
7273 cm⁻¹ (1375 nm) 2 × 2998 plus 1282 cm⁻¹
7752 cm⁻¹ (1290 nm) 2 × 2998 plus 1708 cm⁻¹
8230 cm⁻¹ (1215 nm) 3100 plus 3 × 1708 cm⁻¹
8969 cm⁻¹ (1115 nm) 3 × 2950/2998 cm⁻¹
4.4 OTHER AROMATIC COMPOUNDS

The presence of a heteroatom in an aromatic ring splits the C–H overtone peaks rather than shifting them. For example, in liquid pyridine there is a doublet at each overtone with the lower energy peak attributed to the C–H-stretching absorptions of the 2 and 6 positions, and the higher-energy peak due to the 3, 4, and 5 positions. This is shown in Figure 4.6. These peaks appear at 5835 and 5867 cm\(^{-1}\) (1714 and 1704 nm) for the 2,6-positions, and 5907 and 5956 cm\(^{-1}\) (1693 and 1679 nm) for 3, 4, and 5. Bini et al. suggest that the 3-, 4-, and 5-position peaks appear as only one peak due to overlap.

The highest wavenumber peak in the region near 6000 cm\(^{-1}\) has been assigned by Bini et al. as a combination of two C–H-stretching vibrations, both involving the 2,6-positions. The smaller peaks at 6060, 6105, and 6139 cm\(^{-1}\) are also combinations, of 2,6 and 3,5; 3,5 and 3,5; and 3,5 and 3,5 stretching vibrations.

Figure 4.6 also shows the first combination spectral region of benzene and pyridine near 4500–4700 cm\(^{-1}\). The distinctive set of four large peaks and several smaller ones are considerably shifted for pyridine, relative to benzene. The assignments for these peaks are given in Table 4.1. All are combinations involving a C–H stretch and another vibration.

Thiophene, furan, and pyrrole also have two peaks at each overtone. The spectra of gases of these compounds all shift to higher energy (lower wavelength) relative to the spectra of liquids.
Aromatic Compounds

The second overtones of C–H stretch peaks for liquid pyridine occur at 8785 cm\(^{-1}\) (1138 nm) and 8651 cm\(^{-1}\) (1156 nm). The third and fourth overtones are at 11,296 and 11,474 cm\(^{-1}\) (885 and 872 nm) and 13,810 and 14,037 cm\(^{-1}\) (724 and 712 nm), respectively. The lower frequency band has been assigned to C–H stretches at the 2 and 6 positions, and the higher frequency band was attributed to the C–H stretches at the 3, 4, and 5 positions.

In a study of methyl-substituted pyridines, the aryl regions of the overtones show a simplified structure having one peak progression for each nonequivalent C–H. The methyl regions of the methylpyridines show complex profiles. The band profile in 3- and 4-methylpyridine is similar to that of toluene because the methyl groups of these compounds are free rotors, and all have a low-energy barrier to rotation. However, the methyl band profiles of 2-methylpyridine are complex, and these patterns indicate that vibration-torsional coupling is an important contributor to the complex structure.\(^{10}\)

The near-infrared spectrum of the five-membered ring aromatic organometallic compound ferrocene has also been examined.\(^{11}\) The C–H stretch first overtone of the mid-infrared 3080-cm\(^{-1}\) peak occurs at 6105 cm\(^{-1}\) (1638 nm). A combination peak at 4495 cm\(^{-1}\) (2225 nm) has been assigned as a combination of the 1400-cm\(^{-1}\) C–C stretch mid-infrared peak and the C–H stretch. A doublet centered at 4167 cm\(^{-1}\) (2400 nm) appears to be due to the combination of the asymmetric and symmetric ring-breathing vibrations (1000 and 1100 cm\(^{-1}\) in the mid-infrared) with C–H stretching. Further, a strong peak at 3945 cm\(^{-1}\) (2535 nm) is a combination of the 810-cm\(^{-1}\) C–H bending with the 3080-cm\(^{-1}\) C–H stretch. Lewis also suggested that two smaller peaks observed at

\[\text{FIGURE 4.3 Comparison of benzene (solid curve) and toluene (dotted curve).}\]
FIGURE 4.4 Comparison of benzene (dotted curve) and m-xylene (solid curve) in the $4100 \text{ cm}^{-1}$ region.

FIGURE 4.5 First overtone peak shifting with electronegativity of substituents on benzene ring. (From Weyer, L.G. and Lo, S.-C., in Handbook of Vibrational Spectroscopy, Chalmers, J.C. and Griffiths, P.R., John Wiley & Sons, 2002. With permission.)
Aromatic Compounds

4367 cm\(^{-1}\) (2290 nm) and a broad peak near 4800 cm\(^{-1}\) (2083 nm) are combinations of the C–H stretch with two inactive IR bands at 1257 cm\(^{-1}\) (C–H bend) and 1560 cm\(^{-1}\) (C–C stretch), respectively.

Heterocyclic aromatics with a prominent N–H band include pyrrole and indole where the nitrogen is attached to a single hydrogen. For these compounds, the strong first overtone N–H is apparent at 6835 cm\(^{-1}\) (1463 nm), and the combination band is observed at 4715 cm\(^{-1}\) (2121 nm). The N–H overtone can be shifted by as many as 400 cm\(^{-1}\) when other substituents are present, such as in 2,2-dimethyl-thiazolidine, where the band is observed near 6450 cm\(^{-1}\) (1550 nm). When N–H is present in the heterocyclic compound, a second-overtone bending band may be observed as a very weak shoulder near the 4715-cm\(^{-1}\) (2121-nm) position. Other differences between heterocyclics are found in the C–H region between 6300 cm\(^{-1}\) and 5700 cm\(^{-1}\) (1587 nm to 1754 nm).

REFERENCES


**FIGURE 4.6** Comparison of benzene (dashed) and pyridine (solid) spectra.
5 Hydroxyl-Containing Compounds

5.1 O–H FUNCTIONAL GROUPS

The hydroxyl group has been extensively studied in the near-infrared region, particularly with respect to hydrogen bonding. The advantages of longer pathlength cells for liquids and direct analysis of solids have contributed to the utility of near-infrared for hydrogen-bonding studies in a great variety of mixtures and environments. Also, the near-infrared offers a special advantage over the mid-infrared in the measurement of mixtures of water and other hydroxyl-containing compounds because the combination peaks of water and other hydroxyls are well separated from each other in the near-infrared.

5.2 ALCOHOLS

5.2.1 FIRST OVERTONE REGION

The first overtone of a free hydroxyl group in dilute CCl₄ solution or a low-density gas is at about 7090 cm⁻¹ (1410 nm). This peak is at different positions for primary, secondary, and tertiary alcohols, as seen in Figure 5.1. Primary and secondary butanols can be split into doublets by rotational isomerization.¹ The splits are better seen in Figure 5.2, in the second derivation spectra of the same spectral region. Maeda et al. observed an additional peak in the first overtone region when they subtracted the spectrum at a lower temperature from that at a higher one. They felt that temperature effects further separated species that were weakly bonded to the carbon tetrachloride solvent and a terminal free OH of a self-associated species.

A hydroxyl first overtone peak may also be split due to interactions with the electrons of phenyl rings or halogens, as in benzyl alcohol, for example.

In hydrogen-bonded alcohols, there is a broad peak in the 1460–1600 nm region (6850 cm⁻¹–6240 cm⁻¹), which has been generally attributed to the first overtone of the hydroxyl. This bonded OH peak appears to be broader as a first overtone than its fundamental, as was observed in a series of spectra taken at different temperatures.² On the other hand, the nonbonded OH first overtone is stronger relative to the bonded species than it is in the fundamental, and can be readily detected even when not visible in the fundamental region.³ Figure 5.3 illustrates the differences between the bonded and nonbonded hydroxyls of methanol. The broad bonded OH is indistinct in the neat spectrum, whereas the nonbonded OH in a dilute carbon tetrachloride solution is very sharp and strong.

Temperature- and concentration-dependent variations in self-association of 1-octanol have also been studied by two-dimensional (2-D) Fourier transform near-infrared correlation spectroscopy.⁴ The population of the free OH groups increases with temperature, reportedly reaching 13% at 80°C. The molar absorptivities of the first and second overtones of the monomer were found to be similar in several non-hydrogen-bonding solvents such as carbon tetrachloride, heptane, and octane. The first overtone’s absorptivity was about 1.7 l/mol·cm, which agrees with Goddu’s data.⁵ The absorptivity of the second overtone is about one twentieth that of the first.

Hydrogen bonding of alcohols occurs to different extents with solvents with varying bonding strengths. The spectra of methanol in a series of solvents from carbon tetrachloride through pyridine
The first overtone region exhibits two major bonded OH peaks near 6800 and 7100 cm\(^{-1}\) (14,700 and 1280 nm) when an alcohol is in a solvent capable of hydrogen bonding. Bell and Barrow have shown that the ratio of these two peaks is not affected by temperature or dilution (except for the formation of dimer at very high concentrations). They also show that the second peak is not due to an OH/CH combination band. They suggest that the two peaks are both monomeric hydrogen-bonded-alcohol first overtones, and that the vibrational energy level has been split into two, creating a double minimum in the potential energy curve.

**FIGURE 5.1** First overtone of OH peak in butanols. The dot-dashed curve is isobutanol (a primary alcohol), the dotted curve is 1-butanol, the dashed curve is sec-butanol, and the solid curve is tert-butanol. (From Weyer, L.G. and Lo, S.-C., in Handbook of Vibrational Spectroscopy, Chalmers, J.C. and Griffiths, P.R., John Wiley & Sons, 2002. With permission.)

have been studied.\(^6,7\) The first overtone region exhibits two major bonded OH peaks near 6800 and 7100 cm\(^{-1}\) (14,700 and 1280 nm) when an alcohol is in a solvent capable of hydrogen bonding. Bell and Barrow have shown that the ratio of these two peaks is not affected by temperature or dilution (except for the formation of dimer at very high concentrations). They also show that the second peak is not due to an OH/CH combination band. They suggest that the two peaks are both monomeric hydrogen-bonded-alcohol first overtones, and that the vibrational energy level has been split into two, creating a double minimum in the potential energy curve.

**FIGURE 5.2** Derivative spectra of butanols.
5.2.2 Higher-Order Overtones

The second overtone of the nonbonded OH stretch occurs at about 10,400 cm\(^{-1}\) (960 nm), and the third at about 13,500 cm\(^{-1}\) (740 nm) for simple alcohols. The second overtone has also been used for a number of hydrogen-bonding studies.\(^8\) Variations in the structure of the alcohol result in splitting of the band and systematic shifts. Second overtones of the OH stretch appear to have less interference from CH combination bands than first overtones, and can therefore be more useful for thermodynamic studies.\(^9\) Additional overtones of the nonbonded hydroxyl stretch of alcohols, using gaseous ethanol as a model, are the fourth at 16,700 cm\(^{-1}\) (600 nm) and the fifth at 19,500 cm\(^{-1}\) (510 nm).\(^10\) Additional bonded hydroxyl bands include the OH-stretch second overtone at 9550 cm\(^{-1}\) (1047 nm), a combination of the first overtone of the OH stretch and twice the methyl CH deformation at 9386 cm\(^{-1}\) (1065 nm), and a combination of the OH-stretch first overtone plus three times the CO stretch at 9720 cm\(^{-1}\) (1029 nm).\(^11\)

5.2.3 Combination Bands

A distinctive combination region of alcohols occurs between 4550 and 5550 cm\(^{-1}\) (1800–2200 nm). This broad peak, a combination of OH stretching and OH bending, has been used in a large number of quantitative analyses including hydroxyl number of polymers, alcohols in the presence of water, and ethylene vinyl alcohol content in copolymers. As shown in Figure 5.3, it is present to some extent in both dilute solution and neat spectra of hydroxyl-containing compounds.

In the dilute solution spectrum of methanol, three sharp peaks are observed superimposed on the broader continuum. These can be seen clearly in Figure 5.3. The sharp peaks have been assigned to OH stretch plus CH bending at 5090 cm\(^{-1}\) (1965 nm), OH stretch plus OH bending at 4960 cm\(^{-1}\) (2017 nm), and OH stretch plus CO stretch at 4710 cm\(^{-1}\) (2124 nm).\(^12\) There is also a second combination of OH-stretching and a different OH-bending mode at about 3970 cm\(^{-1}\) (2520 nm). These sharp peaks are at different positions in other alcohols. In the neat spectrum, these peaks are seen as only one broad band centered at about 4770 cm\(^{-1}\) (2100 nm). In the mid-infrared, a diffuse OH association band related to deformation occurs at about 1420 cm\(^{-1}\), which can account for the 4770-cm\(^{-1}\) near-infrared band (1420 cm\(^{-1}\) + 3350 cm\(^{-1}\) = 4770 cm\(^{-1}\)). The diffuse mid-infrared band is said to disappear in dilute solutions of alcohols, where hydrogen...
bonding does not occur.\textsuperscript{13} However, the broad combination peak does not disappear completely in the near-infrared.

There has been some confusion over whether combinations of OH stretch and C–H stretch in the 6330-cm\(^{-1}\) (1580-nm) region contribute to the broad hydrogen-bonded OH overtone peak.\textsuperscript{14,15} Although Kaye appears to assign the 6330-cm\(^{-1}\) peak to this combination, he also says that combination bands involving C–H stretch and OH stretch are very weak because stretching vibrations involving different atoms do not couple well unless their frequencies are nearly the same or the groups involve double bonds or rings. Kaye’s apparent assignment may be simply a function of how one reads his chart, as the two small OH/CH peaks that are observable in his dilute CCl\(_4\) spectrum overlap the broad, bonded OH-stretch first overtone. Figure 5.4 shows the small peaks near the much larger first overtone peak. Bell and Barrow\textsuperscript{16} show that the small peaks (one in ethanol and two in methanol, due to coupling with asymmetric and symmetric C–H stretch) are not present in CD\(_3\)OH dissolved in carbon tetrachloride. Czarnecki et al.\textsuperscript{17} suggest that the series of peaks between 6240 cm\(^{-1}\) (1600 nm) and 7100 cm\(^{-1}\) (1410 nm) are all due to OH-stretch first overtones of different aggregates, such as monomers, dimers, and polymers of the alcohols, but Czarnecki also says in a later article that a band at 6500 is a CH-stretch and nonbonded OH-stretch combination.\textsuperscript{18} Czarnecki et al. found that the 6330-cm\(^{-1}\) peak decreases with temperature when the monomeric 7100-cm\(^{-1}\) peak increases, which supports their theory that it is due primarily to OH overtones. There are apparently contributions from both hydroxyl overtones and CH/OH combinations involved in the broad envelope, although the bonded OH first overtone probably predominates. The evidence of Davies and Rutland does not contradict this statement.

There has also been a suggestion that a 6319-cm\(^{-1}\) (1580-nm) broad peak in ethylene-vinyl alcohol copolymers is due to a combination of OH stretching and 2 OH bending.\textsuperscript{19} However, this peak is generally considered another hydrogen-bonded OH first overtone.

Higher-wavenumber combination bands include one that combines the first overtone of the OH stretch and twice the methyl CH deformation at 9386 cm\(^{-1}\) (1065 nm), and a combination of the OH stretch first overtone plus three times the CO stretch at 9720 cm\(^{-1}\) (1029 nm).\textsuperscript{20}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.4.png}
\caption{OH combination peaks near the much larger first overtone peak.}
\end{figure}
5.3 PHENOLS

5.3.1 OVERTONES

Phenols show absorptions in the same regions as aliphatic alcohols, with first overtones of the O–H near 6940–7140 cm\(^{-1}\) (1400–1440 nm). As seen in Figure 5.5 the first overtone of monomeric phenol in CCl\(_4\) is a single peak at 7040 cm\(^{-1}\) (1420 nm). Ortho-halogens can show a doublet due to \(cis/tran\) isomerism where the \(cis\) form is stabilized by internal hydrogen bonding between the hydroxyl and the halogen.\(^{21,22}\) The \(cis\) form, represented by the large peak shown in Figure 5.5, is shifted to about 6830 cm\(^{-1}\) (1464 nm). The smaller \(trans\) peak is barely discernable in the figure. According to Wheeler, the ratio of the \(cis\) and \(trans\) peaks at different temperatures provides a measure of the stabilizing energy of the \(cis\) form.

The second overtone of dilute phenol in carbon tetrachloride is at 10,000 cm\(^{-1}\) (1000 nm), and the third at 13,250 cm\(^{-1}\) (750 nm). The second and third overtones of the \(o\)-halogenated phenols are doublets due to \(cis/tran\) configurations. For \(o\)-iodophenol, for example, the second overtone peaks are at 9910 and 1029 cm\(^{-1}\) (1009 and 972 nm, respectively), and the third overtones at 12,788 and 13,400 cm\(^{-1}\) (782 and 746 nm, respectively).

Due to the difference in acidity of phenol relative to simple aliphatic alcohols, its spectra in different solvents are quite different from those of methanol and ethanol.\(^{23}\) In solvents of low hydrogen-bonding capability, phenol shows both free and bonded OH first overtones because the solvent cannot bond the phenol completely. In solvents that are more capable of hydrogen bonding, phenol behaves like the alcohols, except that the sequence is accelerated; for example, the spectrum of phenol in \(N, N\)-dimethylformamide appears similar to the spectrum of ethanol in pyridine.

5.3.2 PHENOLS COMBINATIONS

In a study of combination bands of various halogenated phenols, Wulf et al.\(^{24}\) found that most of the combinations involved the OH and bending or twisting modes of the aromatic ring, or the OH group itself. This conclusion was based on the observation that pentachlorophenol, which had no CH groups, showed very similar patterns to the other model species. Rospenk et al.\(^{25}\) compared the spectra of phenol and phenol-OD to show that a series of strong combination bands between

![Figure 5.5 First overtone of phenol in CCl\(_4\) (solid curve) and neat orthochlorophenol (dashed).](image-url)
5210 cm\(^{-1}\) (1920 nm) and 4760 cm\(^{-1}\) (2100 nm) all involve the hydroxyl group but no CH. The 5210-cm\(^{-1}\) and 5080-cm\(^{-1}\) peaks were assigned to OH stretch plus interactions with the ring, the 4949 cm\(^{-1}\) to OH stretch plus OH deformation, and the 4867 cm\(^{-1}\) and 4783 cm\(^{-1}\) were probably due to OH stretch plus C-O stretches with some interactions with other vibrations.26

5.4 MULTIPLE HYDROXYL COMPOUNDS

Glycols and other compounds having more than one hydroxyl have the opportunity for different types of hydrogen bonding. These include many natural compounds such as sucrose, starch, and cellulose. Even in dilute solution, a diol will show an intramolecularly hydrogen-bonded hydroxyl peak.27 Both bonded and nonbonded peaks are observed. The spectrum of 2-methyl-2,4-pentanediol in Figure 5.6 shows a nonbonded peak at 7065 cm\(^{-1}\) (1415 nm) and an intramolecularly bonded peak at about 6850 (1460 nm). A small 6370-cm\(^{-1}\) (1570-nm) intermolecularly bonded peak also appears. Based on information from the fundamental region, it is likely that the spacing between the nonbonded and the intramolecularly bonded peaks increases with the number of carbon atoms between the two hydroxyls.28,29

Carbohydrates in general may have a free OH-stretch absorption near 6940 cm\(^{-1}\) (1440 nm). This band has been reported in crystalline sucrose, for example, and has been assigned specifically to the C\(_4\) hydroxyl within a crystalline matrix.30 Trott et al.31 discuss four different OH first overtone bands in carbohydrates in different solvent systems, using a monomer (glucose) and its polymer (glycogen) as models.

5.5 HYDROPEROXIDES

The first overtone of the nonbonded hydroxyl peak of a hydroperoxide in dilute solution is far enough removed from that of acids and alcohols that it can be used for quantitative analysis.32 The peak is at about 6850 cm\(^{-1}\) (1460 nm) as compared to 7100 cm\(^{-1}\) (1410 nm) for alcohols. The spectrum of cumene hydroperoxide shown in Figure 5.7 shows a splitting of the hydroxyl
Hydroxyl-Containing Compounds

peak due to interaction with the benzene ring. This doublet changes to a singlet in methylene chloride. There is also a combination band that probably involves the OH stretch and OH bending at about 4850 cm\(^{-1}\) (2060 nm), again in dilute solution. These two bands were found to be characteristic of hydrogen peroxides derived from oxidized fatty esters in dilute carbon tetrachloride solutions.\(^{33}\)

Normally, \(\text{H}_2\text{O}_2\) is available as a dilute solution in water, and its OH first overtone is hydrogen bonded and obscured by that of water. However, the combination band near 4850 cm\(^{-1}\) (2060 nm) can be clearly observed, as shown in Figure 5.8.

High overtones of the OH stretch, such as the fifth at 619 nm and the sixth at 532 nm, have been used in studying photoactivated dissociation of t-butyl hydroperoxide.\(^{34}\) Excitation at these wavelengths creates a vibrationally hot electronic ground state.

FIGURE 5.7 Cumene hydroperoxide.

FIGURE 5.8 Hydrogen peroxide solution (solid curve) compared to water (dashed curve).
5.6 OH IN CARBOXYLIC ACIDS

5.6.1 OVERTONES

The OH group associated with monomeric carboxylic acid has a sharp nonbonded or free-stretching first overtone at about 6920 cm\(^{-1}\) (1445 nm). This band has been observed in the high-temperature (92°C) spectrum of octanoic acid.\(^{35}\) As seen in the inset of Figure 5.9, there is some overlap of this band with CH combination bands. This overlap appears more pronounced in acids than in alcohols because the acid hydroxyl absorptivity is significantly lower than the alcohol absorptivity. As the temperature is lowered or the solution becomes more concentrated, the formation of dimers with hydrogen-bonded hydroxyl groups broadens the OH stretch overtone and moves it to a lower frequency (longer wavelength) as it does in the mid-infrared. This is illustrated in Figure 5.9, a temperature series. Although one can usually observe the broad dimeric hydroxyl band in the mid-infrared, in the near-infrared it appears only to shift the baseline upward in the region from about 1700 nm to at least 2200 nm. Spectral subtraction reveals a very broad and shallow curve in this region.

The second overtone of the nonbonded carboxylic acid hydroxyl is at about 10,000 cm\(^{-1}\) (1000 nm), and the third at about 12,500 cm\(^{-1}\) (800 nm).\(^{36}\)

5.6.2 OH IN CARBOXYLIC ACIDS, COMBINATION BANDS

A peak near 5290 cm\(^{-1}\) (1890 nm) due to OH stretch combined with C=O stretch is readily observable in the high-temperature curves of Figure 5.9. Also, a doublet at about 4630 cm\(^{-1}\) (2160 nm) and 4695 cm\(^{-1}\) (2130 nm) can be seen. This is due to a C–H stretch and C=O stretch combination, and has been split because of a rotational mode.

Other, smaller features in the spectrum of monomeric carboxylic acids observed in the gaseous state\(^{37}\) include small peaks near 8200 cm\(^{-1}\) (1220 nm) due to a combination between the first overtone of the OH stretch and a COH bending mode, 8070 cm\(^{-1}\) (1240 nm) due to the first overtone of the OH stretch and the CO stretch, 7600 cm\(^{-1}\) (1315 nm) due to the first overtone of the OH stretch and OCO bending, and 6500 cm\(^{-1}\) (1540 nm) due to OH stretch and C–H stretch.

![FIGURE 5.9 Carboxylic acid hydroxyl peaks. Arrows near 1890 and 2130/2160 point out combination bands relating to the nonbonded hydroxyl. (From Weyer, L.G. and Lo, S.-C., in Handbook of Vibrational Spectroscopy, Chalmers, J.C. and Griffiths, P.R., John Wiley & Sons, 2002. With permission.)](image)
Additional small peaks include those at about 4950 cm\(^{-1}\) (2020 nm), a combination of the OH stretch and CH bending; 4800 cm\(^{-1}\) (2080 nm), the combination of OH stretch and COH bending; 4710 cm\(^{-1}\) (2120 nm), the combination of C–H stretch and C=O stretch; 4680 cm\(^{-1}\) (2140 nm), the combination of OH stretch and CO stretch; 4210 cm\(^{-1}\) (2380 nm), the combination of OH stretch and OCO bending; 4184 cm\(^{-1}\) (2390 nm), the combination of C–H stretch and COH bending; and 4050 cm\(^{-1}\) (2470 nm), the combination of C–H stretch and CO stretch. All of these assignments are for formic acid in the gaseous state. Acids with more complex hydrocarbon structures would have more combination bands, and the region from 4000–4500 cm\(^{-1}\) (2200 nm to 2500 nm) can become quite complex.

Spectra of dimeric carboxylic acids have a different set of small peaks due to the shifts in the OH and C=O structures. In the gaseous spectrum of formic acid, small peaks appear at about 5630 cm\(^{-1}\) (1780 nm) due to a combination of C–H stretch, CH bending, and CO stretch; 4700 cm\(^{-1}\) (2130 nm) due to a combination of C=O stretch and C–H stretch; 4500 cm\(^{-1}\) (2220 nm) due to OH stretch and OH–O bending; 4460 cm\(^{-1}\) (2240 nm) due to OH stretch and CH bending; 4340 cm\(^{-1}\) (2300 nm) due to C–H stretch and OH–O bending; 4310 cm\(^{-1}\) (2320 nm) due to OH stretch and CO stretch; and 4160 cm\(^{-1}\) (2400 nm) due to C–H stretch and COH bending.

### 5.7 SILANOLS

The first overtone of the OH stretch of a silanol group in fused silica optical fibers is at about 7200 cm\(^{-1}\) (1390 nm).\(^3\) See Figure 5.10 for a comparison with water. This band has been resolved into four peaks, two major and two minor, representing three different OH stretch peaks in different environments and one combination with a 280-cm\(^{-1}\) SiO\(_2\) fundamental that is Raman active. The second overtone shows a similar pattern centered at about 10,600 cm\(^{-1}\) (940 nm), and the third near 13,800 cm\(^{-1}\) (725 nm).

Combination band assignments given by Stone and Walrafen\(^3\) for bands at 4100 cm\(^{-1}\) (2440 nm), 4450 cm\(^{-1}\) (2250 nm), and 4520 cm\(^{-1}\) (2210 nm) involve an OH stretch with one of the SiO\(_2\) fundamentals. Combinations involving twice the frequency of an OH stretch with the SiO stretch near 800 cm\(^{-1}\) were noted at 7920 cm\(^{-1}\) (1260 nm) and 8065 cm\(^{-1}\) (1240 nm), and one band at three times an OH stretch plus the 800-cm\(^{-1}\) band was observed at 11,500 cm\(^{-1}\) (850 nm).

![Figure 5.10](image.png)

**FIGURE 5.10** Comparison of silanol bands in silica with those of water.
5.8 ENOLS AND ENOLATES

The enols contain both unsaturated C=\(\text{C}\) double bonds as well as an associated O–H group. These alkene-alcohol and associated anions have the general chemical descriptor as

\[
\begin{align*}
\text{C} \quad \text{OH} \quad \text{C} \\
\text{=} \\
\text{=} \\
\end{align*}
\]

An enolate is an enol-based anion formed by the presence of an enol in a basic medium. An enolate anion, readily formed in the presence of base, is as

\[
\begin{align*}
\text{C} \quad \text{OH} \quad \text{C} \\
\text{=} \\
\text{=} \\
\end{align*} \quad \rightarrow \quad \begin{align*}
\text{C} \quad \text{OH} \\
\text{=} \\
\text{=} \\
\end{align*} \\

\]

Important near-infrared bands associated with enols as phenols are the same as those given for phenols. In Figure 5.11, two example enols as phenols are overlaid from 7200 cm\(^{-1}\) to 3800 cm\(^{-1}\) (1389 nm to 2632 nm). The measured bands associated with phenols include 3\(\nu\) OH as a broad band from 10,200 to 9700 cm\(^{-1}\); 2\(\nu\) OH as a broad band from 7200 to 6000 cm\(^{-1}\); and the \(\nu\) OH + \(\delta\) OH combination envelope located at 5000 to 4500 cm\(^{-1}\). Specific bands associated with enols are very weak and are mainly associated with C=C–H from the aromatic ring. These can be found in the various chapters and spectra demonstrating aromatic and alkene C–H associated -C=C-H bands.

**FIGURE 5.11** Two examples of enols as phenols. The top spectrum is 2-ethyl phenol, and the bottom is 3-methyl phenol. (Spectra used by permission from *NIR Spectra of Organic Compounds*, Wiley-VCH. ISBN 3-527-31630-2.)
REFERENCES


16. Bell, C.L. and Barrow, G.M., op. cit.


23. Bell, C.L. and Barrow, G.M., op. cit.


29. Luck, W.A.P. and Ditter, W., op. cit.

6 Water

6.1 WATER

The analysis of water in various media and under various conditions has been a major part of the field of near-infrared (IR) spectroscopy since its inception. The strength of the near-infrared absorption bands, the unique water combination band at 1940 nm, and the sensitivity of the absorption bands to the environment of the water molecules have all contributed to the success of near-infrared to study and measure water.

6.2 LIQUID WATER, ICE, AND WATER VAPOR

A summary of the absorption bands of water in the 800–2500-nm region is provided in Table 6.1. The vapor spectral details shown in the table were probably taken from a low-resolution spectrum, as a much larger number of water-vapor peaks have been reported by others. As shown in the table, the accepted assignments for the two bands at about 6900 cm⁻¹ (1450 nm) and 10,300 cm⁻¹ (970 nm) indicate that these are combination bands involving the symmetric and asymmetric stretching modes of the water molecule. This observation has been made by comparison with high-resolution vapor spectra, which show that the combination bands are stronger than the overtones of either the symmetric or asymmetric stretch. This assignment is further supported by consideration of the symmetry group of the vibrations. It has also been suggested that the first overtone of the asymmetric stretch is accidentally degenerate with the sum of asymmetric and symmetric stretches in dilute solutions. Therefore, although these two bands are generally referred to as the first and second overtones of the OH stretch, they are actually combination bands.

The strong 5150-cm⁻¹ (1940-nm) peak is a combination of the asymmetric stretch and bending of the water molecule. In liquid water, there also are weak, broad combination bands near 5620 cm⁻¹ (1780 nm) and 8310 cm⁻¹ (1200 nm), and a second set near 11,800 and 13,000 cm⁻¹ (840 and 740 nm, respectively).

The water peaks with maxima near 10,300 cm⁻¹ (970 nm), 8330 cm⁻¹ (1200 nm), and 6900 cm⁻¹ (1450 nm) at room temperature shift towards higher wavenumber (lower wavelength) with increasing temperature, and appear to consist of an unresolved pair of peaks with an isosbestic point between them. See Figure 6.1 for an illustration of the temperature effect at the “first overtone.” The isosbestic point for the 10,300-cm⁻¹ (970-nm) band is 10,100 cm⁻¹ (990 nm), for the 8330-cm⁻¹ (1200-nm) band is about 8400 cm⁻¹ (1190 nm), and for the 6900-cm⁻¹ (1450-nm) band is at about 6960 cm⁻¹ (1440 nm). The presence of an isosbestic point indicates that NIR calibrations for water independent of temperature may be possible by judicious wavelength choice.

An isosbestic point has also been studied for pressure changes of water at constant temperature. A shift to higher wavenumber (lower wavelength) occurred with increasing pressure. The pressure isosbestic point for the 10,300-cm⁻¹ peak was at about 10,200 cm⁻¹ (980 nm).

There has been some controversy over whether liquid water contains water molecules in three states of hydrogen bonding: free; bonded through one, two, or three hydrogen bonds; or a continuum of different bond strengths or somewhere in between. In general, temperature studies and data
treatments such as second derivatives and spectral resolution have indicated that there are separate peaks present for different states of hydrogen-bonded water molecules. As pointed out by Maeda et al., the intensities and width of these peaks are affected by the anharmonicity of each, so that the molecules bonded to more adjacent molecules, having less anharmonicity, will be broader and weaker.

Figure 6.2 and Figure 6.3 show the spectra of liquid water and water in a “free” state, in carbon tetrachloride.

TABLE 6.1
Absorption Peaks of Water, Ice, and Vapor

<table>
<thead>
<tr>
<th>Ice (nm)</th>
<th>Ice (cm⁻¹)</th>
<th>Liquid Near Freezing Point (nm)</th>
<th>Liquid Near Freezing Point (cm⁻¹)</th>
<th>Liquid Near Boiling Point (nm)</th>
<th>Liquid Near Boiling Point (cm⁻¹)</th>
<th>Vapor (nm)</th>
<th>Vapor (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>12,500</td>
<td>770</td>
<td>13,000</td>
<td>740</td>
<td>13,500</td>
<td>723</td>
<td>13,831</td>
<td>3 ν₁+ ν₃</td>
</tr>
<tr>
<td>909</td>
<td>11,000</td>
<td>847</td>
<td>11,800</td>
<td>840</td>
<td>11,900</td>
<td>823</td>
<td>12,151</td>
<td>2 ν₁+ ν₂+ ν₃</td>
</tr>
<tr>
<td>1025</td>
<td>9760</td>
<td>979</td>
<td>10,210</td>
<td>967</td>
<td>10,340</td>
<td>942</td>
<td>10,613</td>
<td>2 ν₁+ ν₅</td>
</tr>
<tr>
<td>1250</td>
<td>7990</td>
<td>1200</td>
<td>8310</td>
<td>1160</td>
<td>8640</td>
<td>1135</td>
<td>8807</td>
<td>ν₁+ ν₂+ ν₃</td>
</tr>
<tr>
<td>1492</td>
<td>6700</td>
<td>1453</td>
<td>6880</td>
<td>1425</td>
<td>7020</td>
<td>1380</td>
<td>7252</td>
<td>ν₁+ ν₃</td>
</tr>
<tr>
<td>1780</td>
<td>5620</td>
<td>1780</td>
<td>5620</td>
<td>1786</td>
<td>5600</td>
<td>—</td>
<td>—</td>
<td>ν₁+ ν₂+ ν₅</td>
</tr>
<tr>
<td>1988</td>
<td>5030</td>
<td>1938</td>
<td>5160</td>
<td>1916</td>
<td>5220</td>
<td>1875</td>
<td>5332</td>
<td>ν₂+ ν₃</td>
</tr>
</tbody>
</table>

Note: For this table, ν₁ is the symmetric stretch of the water molecule, ν₂ is the bending mode, and ν₃ is the asymmetric stretch. ν₅ was not defined in the original reference. It has been postulated to be an “intermolecular mode.”

FIGURE 6.1 Water spectra at four temperatures from 25 to 65°C.
6.3 DEUTERIUM OXIDE (D₂O)

The near-infrared spectrum of fully deuterated water is very similar to that of H₂O, except that the peaks are all shifted because of the mass difference of the hydrogen atom. Table 6.2 summarizes the absorptions. Figure 6.4 shows a portion of the near-infrared spectral region, illustrating the isotope shift of the \( \nu_1 + \nu_3 \) combination band (indicated by stars).

HDO is not of the same symmetry group as H₂O and D₂O, and therefore its peak shifts are not strictly isotope shifts. Also, liquid HDO is in equilibrium with H₂O and D₂O, and the contributions
Practical Guide to Interprettive Near-Infrared Spectroscopy

from these molecules must be subtracted in order to observe the spectrum of HDO. Note that the large combination band used most often for moisture measurement is out of the normal NIR range for deuterium oxide.

6.4 WATER IN VARIOUS SOLVENTS

The structure of water and the band assignments of water in various solvents have been studied extensively in the NIR. The 5155-cm\(^{-1}\) (1940-nm) combination band in particular has been very useful for studies and analyses of water in the presence of hydroxyl-containing solvents because it is usually well isolated.

Interactions are strongest in dimethyl sulfoxide (DMSO) and weakest in nitromethane, as demonstrated by the position of the 5155-cm\(^{-1}\) (1940-nm) peak. The series of solvents includes, in order, DMSO, dioxane, acetone, acetonitrile, and nitromethane, and the peak maximum ranged from 5150 cm\(^{-1}\) (1942 nm) to 5270 cm\(^{-1}\) (1898 nm). The effect of low levels of ethanol added to water was seen to be qualitatively the same as a temperature effect.

![Figure 6.4](image)

**FIGURE 6.4** Comparison of water and deuterium oxide. The dotted curve is water, and the solid curve is deuterium oxide. Stars indicate the \(\nu_1 + \nu_3\) combination band in both.

### TABLE 6.2
Band Assignments for H\(_2\)O, D\(_2\)O, and HDO

<table>
<thead>
<tr>
<th>Liquid H(_2)O Near Freezing Point (nm)</th>
<th>Liquid H(_2)O Near Freezing Point (cm(^{-1}))</th>
<th>Liquid D(_2)O (nm)</th>
<th>Liquid D(_2)O (cm(^{-1}))</th>
<th>Liquid HDO (nm)</th>
<th>Liquid HDO (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>770</td>
<td>13,000</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>(3\ \nu_1 + \nu_3)</td>
</tr>
<tr>
<td>847</td>
<td>11,800</td>
<td>1190</td>
<td>8400</td>
<td>1000</td>
<td>10,000</td>
<td>(2\ \nu_1 + \nu_2 + \nu_3)</td>
</tr>
<tr>
<td>979</td>
<td>10,210</td>
<td>1340</td>
<td>7470</td>
<td>1240</td>
<td>8065</td>
<td>(2\ \nu_1 + \nu_3)</td>
</tr>
<tr>
<td>1200</td>
<td>8310</td>
<td>1620</td>
<td>6165</td>
<td>-</td>
<td>-</td>
<td>(\nu_1 + \nu_2 + \nu_3)</td>
</tr>
<tr>
<td>1453</td>
<td>6880</td>
<td>1970</td>
<td>5080</td>
<td>1670</td>
<td>5975</td>
<td>(\nu_1 + \nu_3)</td>
</tr>
<tr>
<td>1780</td>
<td>5620</td>
<td>2440</td>
<td>4100</td>
<td>-</td>
<td>-</td>
<td>(\nu_2 + \nu_3 + \nu_L)</td>
</tr>
<tr>
<td>1938</td>
<td>5160</td>
<td>2600</td>
<td>3830</td>
<td>2020</td>
<td>4945</td>
<td>(\nu_2 + \nu_3)</td>
</tr>
</tbody>
</table>
In all solvents, the fraction of free water was greater in both dilute solution and in neat water than it was in intermediate concentrations. Through the analysis of ternary mixtures, the amount of nonbonded water molecules was found to be negligibly small in proton-acceptor solvents.

6.5 WATER IN OTHER MATRICES, INCLUDING GLASSES

The relative position of the water bands has provided a good deal of information to researchers. In studying protein denaturation, for example, the symmetric stretch plus asymmetric stretch combination band provided information on the state of the water during the reaction. The shift from 1410 to 1490 nm indicated an increase in bound water.\(^{19}\) In studying water sorption on PET film, the same spectral region showed that water was not interacting with the film. The wavelengths of the sub-bands in that region were all lower than those in bulk water.\(^{20}\) The total water content of starch and cellulose was compared to the “water activity” using the 1450- and 1940-nm bands.\(^{21}\) It was found that NIR could discriminate between different levels of moisture content at the same activity but not very well between activities at the same moisture content. The 1940-nm band was also used in a cell adhesion study.\(^{22}\)

Water incorporated into fused silica is of considerable importance because the resulting silanol groups affect the NIR transmission of silica optical fibers and other optical components. Silanols are discussed in the OH section. In mixed glasses, such as those containing borosilicates, aluminosilicates, and so on, associated water OH groups give rise to diffuse absorption bands.\(^{23}\) The absorption bands of water molecules on silica surfaces have been described by Klier et al.\(^{24}\)

6.6 IONIC SPECIES IN WATER

There are several ways that ionic species in water affect near-infrared spectra. These affects include (1) a decrease in the concentration of water, (2) charge-dipole interactions between the ions and the water molecules that affect the hydrogen bonding of the water itself, (3) the formation of hydrogen bonds between an oxygen or nitrogen in the ions and water, (4) the presence of OH itself or OH within an ion (such as HCO\(_3^−\)), and (5) the presence of another specific NIR-active functional group within the ion (such as acetate’s CH and ammonia’s NH), and the condition by which some ions produce OH or H through hydrolysis (such as CO\(_3^{2−}\)).\(^{25}\) In addition, the color of some ions can extend into the NIR region.

One example of an ionic interaction with water molecules is shown in Figure 6.5. Sodium chloride alone in water can be readily measured in spite of its having no NIR bands of its own because it

FIGURE 6.5 The effect of dissolved sodium chloride on the water spectrum. The solid curve is pure water, whereas the dotted curve is 20% NaCl.
affects the spectrum of water by reducing the amount of hydrogen bonding within the bulk water.26,27 The salt lowers the intensity of the water peak and also shifts it to the left, toward higher frequencies, indicating less hydrogen bonding.

Different ions have somewhat different effects, depending on their size and electronic characteristics. Thermodynamic calculations have indicated that divalent magnesium ions, trivalent aluminum ions, and protons enhance the structural order of the water, whereas monovalent sodium and potassium disrupt it.28 Differences in the intensities of changes to the near-infrared spectra have been attributed to the charge-to-radius ratios of cations or anions.29 An example of the effect of a proton is shown in the HCl spectrum in Figure 6.6. Note the shift towards lower wavenumber, indicating an increase in hydrogen bonding. Hydroxide and fluoride anions are said to enhance the structure, whereas chloride, bromide, nitrite, and isocyanate disrupt it.30 Choppin and Buijs based their assessment of structure effects on the 8330-cm$^{-1}$ (1200-nm) combination band by calculating the relative intensities of the free, singly bonded, and doubly bonded peaks. Measurements of pH and titration endpoints by NIR based on the effects on the water peaks have been reported.31

**FIGURE 6.6** Spectrum of concentrated HCl (dotted curve) compared to pure water in a 0.5-mm pathlength cell.

**FIGURE 6.7** Sodium hydroxide solutions, 0–50% NaOH. The bottom curve is 50% NaOH, and the top is 100% water.
The ionic hydroxyl group in aqueous solutions has its own specific absorption bands with first and second overtone bands at 7040 cm\(^{-1}\) (1421 nm) and 1034 cm\(^{-1}\) (967 nm), respectively.\(^3\) Also, a broad band centered at about 1100 nm has been attributed to the binding of two water molecules to the hydroxide ion. As the hydroxide concentration is increased above 5 molal, the water peaks at 6900 cm\(^{-1}\) (1450 nm) and 1025 cm\(^{-1}\) (976 nm) decrease, and the hydroxide ion peaks at 1421 and 967 nm become prominent. This effect is complicated, however, and involves water activity and the ability of the solutes to confine the bulk solvent within hydration spheres. KOH solutions do not behave the same as NaOH solutions, and the effects of the cation on the water absorption need to be accounted for to obtain good measurements of hydroxide. Figure 6.7 illustrates the prominent ionic hydroxyl peak near 7040 cm\(^{-1}\) (1421 nm). It is especially noticeable in the 50% solution.

REFERENCES

29. Lin, J. et al., op. cit.
31. Molt, K. et al., op. cit.
7 Carbonyls

7.1 ORGANIC CARBONYL COMPOUNDS, OVERTONES

Aldehydes, ketones, esters, anhydrides, acid chlorides, and carboxylic acids show some near-infrared carbonyl-associated bands, as illustrated in Figure 7.1. The C=O stretch is very strong in the mid-infrared, so, even though the first overtone is still in the mid-infrared region, the second overtone may be strong enough to observe in the near-infrared. Although the second overtones are relatively weak and would be overwhelmed if any water were present, there are some anhydrous situations in which it might be useful to analyze carbonyl compounds by near-infrared spectroscopy.

As in the mid-infrared, the position of the C=O varies with the environment of the group. The position or frequency of the fundamental carbonyl C=O stretching vibration is affected by (1) the isotope effects and mass change of substituted groups, (2) bond angles of substituted groups, (3) electronic (resonance and inductive) effects, and (4) interactions of these effects. Substituents with higher mass decrease the C=O stretch frequency; increasing the mass or bond angles of substituents also decreases the fundamental band frequency by up to 40 cm\(^{-1}\) at 1715 cm\(^{-1}\). Similarly, decreasing the substituent mass, or bond angles between the carbonyl carbon and its substituents, increases the frequency by 25 cm\(^{-1}\) above the nominal 1715-cm\(^{-1}\) carbonyl C=O stretch frequency. More electronegative (electron-withdrawing) substituents will increase the carbonyl carbon–oxygen stretch frequency by up to 100 cm\(^{-1}\) above the 1715-cm\(^{-1}\) nominal frequency. Conjugation of the carbonyl group to aromatic or olefinic groups tends to lower the frequency for both C=O and C=C by 30 to 40 cm\(^{-1}\), depending upon the ring size of the substituent.

In general, the position of the second overtone of the carbonyl of simple noncyclic aliphatic compounds shifts to lower wavelength in the series: acid chlorides, anhydrides, carboxylic acid monomer, lactones, aldehydes, ketones, and esters. Amide carbonyl second overtones are overwhelmed by bands that involve NH stretch and cannot therefore be included in this comparison. An acid chloride second overtone is at 5400 cm\(^{-1}\) (1850 nm), propionaldehyde is at 5100 cm\(^{-1}\) (1960 nm), acetone is at 5100 cm\(^{-1}\) (1960 nm) (with an additional split band at 5260 cm\(^{-1}\) [1900 nm]), and ethyl acetate is at 5160 cm\(^{-1}\) (1940 nm).

Conjugation with aromatic rings and double bonds, and interactions with halogens and cyclic structures, all affect the band positions, as in the mid-infrared. Also, these second overtones are sometimes split into two as there may be two or more small bands in the vicinity of the calculated second overtone.\(^1\) The second overtone of the C=O of a carboxylic acid appears at about 5260 cm\(^{-1}\) (1900 nm) and is particularly clear in a spectrum of perfluorocaproic acid taken in solution, as this acid has no CH absorptions.\(^2\) It can be seen in Figure 7.2, a comparison between octanoic and octadecanoic acids in carbon tetrachloride. With the shorter-chain acid, the acid carbonyl peak is more prominent.

The C–H stretch overtones of aldehydes should be observed at shorter wavenumbers than most compounds as they are in the mid-infrared. They are not very distinctive, however. In the mid-infrared region, the C–H stretch is usually a doublet and involves interaction with an overtone of a bending mode.\(^3\) Therefore, it is not likely to be very strong in the near-infrared. The C–H stretch of benzaldehyde’s alkyl is at 5376 cm\(^{-1}\) (1860 nm).\(^4\) It is very weak, possibly due to perturbation by a combination band.
7.2 ORGANIC CARBONYL COMPOUNDS, COMBINATION BANDS

In addition to the overtones, there are some combination bands that include the C=O stretch. Combination bands involving C=O and CH in ketones are weak, if they exist at all, because the two groups do not share a common carbon atom. In aldehydes and formates, however, there is a carbon atom with both a proton and an oxygen atom attached, which gives rise to a combination band in the region of 4760 to 4445 cm\(^{-1}\) (2100–2200 nm).\(^5\)\(^6\) The strong formate ester band at 4650 cm\(^{-1}\) (2150 nm) was assigned to C–H stretch and C=O stretch by a deuteration study.\(^7\)

**FIGURE 7.1** Comparison of different types of carbonyl compounds. *Note:* The solid curve is neat propionaldehyde, dashed curve is ethyl acetate in CCl\(_4\), dotted curve is neat acetone; arrows indicate the carbonyl second overtone doublets, and stars indicate combination bands involving the carbonyls.

**FIGURE 7.2** Illustration of acid carbonyl second overtone; octanoic acid (dotted curve) and octadecanoic acid (solid).
In one study of short-chain aliphatic aldehydes, the C–H stretch + C=O stretch combination band was given as a peak at 4504 cm\(^{-1}\) (2220 nm) and a 2 × CH bend (in-plane rocking) plus the carbonyl stretch at about 4514 cm\(^{-1}\) (2215 nm). These appear to be one peak in Figure 7.3. Also a peak near 4888 cm\(^{-1}\) (2045 nm) was assigned as 2 × C=O stretch plus 2 × CH bending (out-of-plane wagging), and one at 4748 cm\(^{-1}\) (2106 nm) was assigned as a combination of CH bending (in-plane rocking) and C=O stretching. Figure 7.3 illustrates these absorption peaks. There is also an aldehyde-associated peak near 7850 cm\(^{-1}\), as seen in Figure 7.4, and aldehyde spectra.
found in the appendices. This could be a second overtone involving the 2700-cm\(^{-1}\) fundamental CH peak. However, the fundamental C–H stretch absorption is split by Fermi resonance, and therefore, near-infrared peaks are probably also complicated by Fermi resonance.

### 7.3 CARBONATE

The inorganic ion CO\(_3\)\(^{2-}\) has been analyzed in the near-infrared region in many geological studies. It has two strong bands of particular usefulness near 3920 and 4255 cm\(^{-1}\) (2550 and 2350 nm, respectively). The 3920-cm\(^{-1}\) band is most likely due to the sum of an infrared-forbidden symmetric stretch and twice the asymmetric stretch (\(\nu_1 + 2\nu_3\)). The 4255-cm\(^{-1}\) band has been assigned as the second overtone of the strong asymmetric stretch (3\(\nu_3\)).\(^{10,11}\) Figure 7.5 shows the strong 4255-cm\(^{-1}\) (2350-nm) band clearly.

The band positions shift with environment and are in different positions in calcium carbonate (polymorphs calcite and aragonite), dolomite (calcium magnesium carbonate), sodium carbonate, and so on, alone or in aqueous solutions.

### 7.4 ISOCYANATES

Table 7.1 provides some band assignments made for the isocyanate group N\(=\)C=O.\(^{12}\)

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Wavelength (nm)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>4872</td>
<td>2052</td>
<td>2 (\times) (\delta) (NCO) + (\nu) (NCO)</td>
</tr>
<tr>
<td>5220</td>
<td>1915</td>
<td>(\nu) (NCO) + (\nu) CH</td>
</tr>
</tbody>
</table>

FIGURE 7.5 Reflection spectrum of powdered calcium carbonate.
REFERENCES

6. Holman, R.T. and Edmondson, P.R., op. cit.
8 Amines and Amides

8.1 N–H FUNCTIONAL GROUPS

The N–H functional group found in amines and amides has not been studied as extensively as hydroxyls, but it is important because it appears in many natural products, pharmaceuticals, and polymers. N–H participates in hydrogen bonding and therefore behaves differently in various solvents and matrices. The near-infrared region offers a special advantage in the measurement of the primary amine group NH$_2$ due to a unique combination band.

8.2 AMINES, ALIPHATIC

8.2.1 OVERTONES

As shown in Figure 8.1, primary and secondary amines are distinctly different in the first overtone region near 6600 cm$^{-1}$. Primary amines have a doublet, and secondary a single peak. Tertiary amines have no peak as they have no N–H functionality and are not shown in the figure. The asymmetric and symmetric NH-stretching peaks occur at 6553 and 6730 cm$^{-1}$ (1625 and 1486 nm), respectively, in butyl amine in carbon tetrachloride. The first overtone of secondary amines has only one band near 6530 cm$^{-1}$ (1530 nm).

Figure 8.1 shows a primary and a secondary amine in dilute carbon tetrachloride solution. The NH-stretch first overtones broaden and shift to longer wavelengths with an increase in concentration, and shift slightly in other solvents. It has been reported that the band position does not change with temperature in the range of 70–120°C in contrast with the hydroxyl group. The symmetric absorption of the –NH$_2$ group is much more intense (~6 to 7 times) than the asymmetric absorption.

Polar groups next to the amine tend to displace the first overtone. An amine next to phosphorus has its first overtone at 6720 cm$^{-1}$ (1488 nm) and 7652 cm$^{-1}$ (1481 nm).

In the mid-infrared region, the amine NH-stretch absorption is weak relative to primary alcohols, about 1–2 l/mol-cm compared to 50–100 l/mol-cm. However, the intensity of the first overtone of aliphatic amines is of the same order of magnitude as the fundamental. For example, n-butyl amine’s first overtone has an absorptivity of 0.6 l/mol-cm compared to 2.4 l/mol-cm for the fundamental. The overtones of amines and hydroxyls are of approximately the same magnitude, and it may be easier to detect an amine in the presence of alcohols in the near-infrared than the mid-infrared.

A single peak that occurs near 9700 cm$^{-1}$ (1035 nm) has been assigned to the second overtone of –NH$_2$. The third overtone occurs as a doublet at 12,407 and 12,837 cm$^{-1}$ (806 and 779 nm). The absorption of the latter band is also stronger, and its intensity increases with increasing chain length. The fourth overtone appears as a doublet near 15,129 cm$^{-1}$ (661 nm), but one of the pair is of much lower intensity.

8.2.2 COMBINATIONS

The first combination band region of primary amines, which derives from the N–H-stretching modes and the deformation or scissoring of the NH$_2$ group, has been found to be very useful in quantitative and qualitative analyses. As shown in Figure 8.1, n-butyl amine has a strong doublet in CCl$_4$ near 5000 cm$^{-1}$ that is totally absent in secondary (or tertiary) amines. This feature is not a doublet in all solvents, and its dual nature has been attributed to interaction with the solvents. It is a single peak in benzene and hexane but a double peak in mixtures of benzene and chloroform. The lower frequency peak increases upon addition of more polar solvents, and its position has been used to
study solvent associations. Sinsheimer and Keuhnelian have interpreted the doublet as being due to a free (higher wavenumber) and a hydrogen-bonded band (lower wavenumber). A second set of combination bands has been reported at 12,000 and 12,380 cm$^{-1}$ (832 and 808 nm) in secondary amines.

8.3 AMINES, AROMATIC
8.3.1 OVERTONES

The NH-stretching bands of aromatic amines such as aniline show a doublet in the first overtone region, but it is shifted to lower wavelengths relative to aliphatic amines. Figure 8.2 compares the near-infrared spectrum of aniline in CCl$_4$ with that of n-butyl amine. The asymmetric vibration occurs...
Amines and Amides

at 6890 cm\(^{-1}\) (1450 nm), and the symmetric band is in the region of 6685 cm\(^{-1}\) (1496 nm). In studies of ring-substituted derivatives, Whetsel\(^{10}\) has investigated the correlation of a substituent electronic nature with band positions and intensities in both NH-stretching and combination modes. The shifts of NH overtone bands may be observed as effects of various solvents and temperature conditions.

As in the case of the aliphatic amines, secondary aromatic amines show only one NH-stretching overtone. For \(N\)-butyl aniline in CCl\(_4\), for example, the overtone is at 6675 cm\(^{-1}\) (1498 nm). The effects of hydrogen bonding on the mechanical anharmonicity of the NH-stretching vibration of \(N\)-methylaniline have been reported.\(^{11}\)

In heterocyclic aromatic amines such as pyrrols, indoles, and carbazoles, there is a first overtone NH-stretching between 6803 cm\(^{-1}\) (1470 nm) and 6897 cm\(^{-1}\) (1440 nm).\(^{12}\) Unlike the aliphatic amines, where the intensity of the overtone is approximately the same as the intensity of the fundamental, the aromatic and heterocyclic amines have a much greater absorptivity difference between fundamental and overtone. The overtone intensities do not vary widely, but the intensities of the fundamentals vary by a factor of about 100 from aliphatic to heterocyclic. Table 8.1 lists some of the intensities, given in integrated peak area.

Table 8.2 lists band positions and intensities of some primary aromatic amines in carbon tetrachloride, illustrating the effect of substituents.\(^{13}\) The table also includes the second overtone

### Table 8.1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Area of Fundamental (\times 10^9)</th>
<th>Area of First Overtone (\times 10^9)</th>
<th>Ratio of Areas</th>
<th>Position of Overtone (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylamine (vapor)</td>
<td>~6</td>
<td>9.5</td>
<td>~0.6</td>
<td>6580</td>
</tr>
<tr>
<td>Diethylamine</td>
<td>~3.5</td>
<td>~4.8</td>
<td>~0.7</td>
<td>6471</td>
</tr>
<tr>
<td>Morpholine</td>
<td>21</td>
<td>10</td>
<td>2.1</td>
<td>6536</td>
</tr>
<tr>
<td>Dibenzylamine</td>
<td>30</td>
<td>6.2</td>
<td>4.9</td>
<td>6490, 6512, 6534</td>
</tr>
<tr>
<td>(N)-benzylamine</td>
<td>183</td>
<td>7.5</td>
<td>24</td>
<td>6751</td>
</tr>
<tr>
<td>Diphenylamine</td>
<td>228</td>
<td>5.6</td>
<td>40</td>
<td>6729</td>
</tr>
<tr>
<td>Indole</td>
<td>568</td>
<td>11.2</td>
<td>59</td>
<td>6844</td>
</tr>
<tr>
<td>Carbazole</td>
<td>550</td>
<td>8.8</td>
<td>62</td>
<td>6826</td>
</tr>
</tbody>
</table>

*Note: CCl\(_4\) solution. Area in units of cm\(^2\) mol\(^{-1}\) sec\(^{-1}\)*

### Table 8.2

<table>
<thead>
<tr>
<th>Substituent</th>
<th>First Overtone Symmetric (cm(^{-1}))</th>
<th>First Overtone Symmetric (nm)</th>
<th>First Overtone Asymmetric (cm(^{-1}))</th>
<th>First Overtone Asymmetric (nm)</th>
<th>Second Overtone (cm(^{-1}))</th>
<th>Second Overtone (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(p)-NH(_2)</td>
<td>6656</td>
<td>1502.5</td>
<td>6852</td>
<td>1459.5</td>
<td>9741</td>
<td>1026.5</td>
</tr>
<tr>
<td>(p)-CH(_3)</td>
<td>6683</td>
<td>1496.5</td>
<td>6885</td>
<td>1452.5</td>
<td>9775</td>
<td>1023.0</td>
</tr>
<tr>
<td>None</td>
<td>6698</td>
<td>1493.0</td>
<td>6904</td>
<td>1448.5</td>
<td>9794</td>
<td>1021.0</td>
</tr>
<tr>
<td>(p)-Cl</td>
<td>6705</td>
<td>1491.5</td>
<td>6906</td>
<td>1448.0</td>
<td>9813</td>
<td>1019.0</td>
</tr>
<tr>
<td>(m)-Cl</td>
<td>6713</td>
<td>1489.5</td>
<td>6920</td>
<td>1445.0</td>
<td>9818</td>
<td>1018.5</td>
</tr>
<tr>
<td>(m)-NO(_2)</td>
<td>6725</td>
<td>1487.0</td>
<td>6940</td>
<td>1441.0</td>
<td>9852</td>
<td>1015.0</td>
</tr>
<tr>
<td>(o)-OCH(_3)</td>
<td>6700</td>
<td>1492.5</td>
<td>6916</td>
<td>1446.0</td>
<td>9818</td>
<td>1018.5</td>
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<tr>
<td>(o)-Cl</td>
<td>6705</td>
<td>1491.5</td>
<td>6930</td>
<td>1443.0</td>
<td>9828</td>
<td>1017.5</td>
</tr>
<tr>
<td>(o)-NO(_2)</td>
<td>6791</td>
<td>1472.0</td>
<td>6982</td>
<td>1432.0</td>
<td>9970</td>
<td>1003.0</td>
</tr>
</tbody>
</table>
band positions. Molar absorptivities, generally around 1.3 l/mol-cm for the symmetric band, around 0.15 l/mol-cm for the asymmetric, and 0.03 l/mol-cm for the second overtone, were also provided in the reference.

The self-association of aromatic amines in various solvents and temperatures has been studied extensively and has been summarized by Whetsel.\(^{14}\) The formation of dimers and higher-order associations has been proposed. Association in carbon tetrachloride occurs and some authors have found chloroform to be a better choice for analyzing amines in general.

### 8.3.2 Combinations

The band near 5070 cm\(^{-1}\) (1972 nm) is due to a combination of NH stretching and bending. A number of examples of band positions are included in Table 8.3.

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Combination band (cm(^{-1}))</th>
<th>Combination band (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-NH(_2)</td>
<td>5049</td>
<td>1980.5</td>
</tr>
<tr>
<td>p-CH(_3)</td>
<td>5062</td>
<td>1975.5</td>
</tr>
<tr>
<td>None</td>
<td>5072</td>
<td>1971.5</td>
</tr>
<tr>
<td>p-Cl</td>
<td>5075</td>
<td>1970.5</td>
</tr>
<tr>
<td>m-Cl</td>
<td>5082</td>
<td>1968.0</td>
</tr>
<tr>
<td>m-NO(_2)</td>
<td>5095</td>
<td>1965.0</td>
</tr>
<tr>
<td>o-CH(_3)</td>
<td>5057</td>
<td>1977.5</td>
</tr>
<tr>
<td>o-Cl</td>
<td>5072</td>
<td>1971.5</td>
</tr>
<tr>
<td>o-NO(_2)</td>
<td>5084</td>
<td>1967.0</td>
</tr>
</tbody>
</table>

![FIGURE 8.3](image)

**FIGURE 8.3** NIR spectrum of ammonia in water (bottom) compared to water itself (top). The top curve is 5% ammonium hydroxide in water. The dotted curve is pure water, and the bottom curve shows the difference between the two, slightly expanded to accentuate the peaks.
8.4 AMMONIA

Ammonia, being a weak base, is primarily in the form of NH₃ in water, and its spectrum resembles that of an amine. Ammonia in water shows strong bands at 6520 cm⁻¹ (1534 nm), 5000 cm⁻¹ (2000 nm), and 4525 cm⁻¹ (2210 nm) in addition to water bands. See Figure 8.3. The first overtone near 6520 cm⁻¹ appears as a single peak even in gaseous ammonia. In fact, gaseous ammonia has been recommended as a wavelength standard for near-infrared spectrometers. In a 10-cm cell, bands at 6609 cm⁻¹ (1513 nm), 5084 cm⁻¹ (1967 nm), and 4417 cm⁻¹ (2264 nm) were cited.

There is also a sharp second overtone peak at about 9560 cm⁻¹ (1046 nm), as shown in Figure 8.4.

8.5 AMIDES, ALIPHATIC AND AROMATIC

8.5.1 OVERTONES

Near-infrared spectra of primary amides (RCO-NH₂), such as formamide, acetamide, and benzamide, have been studied in chloroform solution. Two bands at 6710 cm⁻¹ (1490 nm) and 6995 cm⁻¹ (1430 nm) have been assigned to first overtones of the asymmetric and symmetric N–H stretching modes.

The assignment of secondary amides has also been studied extensively. A single band between 6711 and 6803 cm⁻¹ (1470 to 1490 nm) for N-methyacacetamide and other simple amides was attributed to the first overtone NH stretch. Dilute solutions of N-methylacetamide in either carbon tetrachloride or water have a band at 6711 cm⁻¹ (1470 nm), whereas more concentrated solutions have a doublet in the 6666–6880-cm⁻¹ (1500–1700-nm) range. In CCl₄, the bonded doublet appears at concentrations above 1 M, whereas in water the unassociated band is present until about 8 M.

When the fundamental and first overtone NH-stretch absorptions of secondary amides are compared, it is observed that the relative intensities of the free and bound peaks are very different. As seen in Figure 8.5, the overtone of the “free” NH is relatively stronger in the first overtone when compared to the fundamental. This is because hydrogen bonding has increased the anharmonicity of the vibration, resulting in the higher-intensity overtone.

As in amines, the first overtone of OH- and NH-stretching absorptions are comparable in intensity, whereas in the fundamental region the OH is much stronger. A comparison of OH and NH first overtone peak intensities can be seen in Figure 8.6. The figure illustrates the reaction of phenol with an isocyanate to form an amide.

**FIGURE 8.4** Low-wavelength region of 10% ammonia in water (solid curve) compared to water (dotted curve).
The second overtone of primary amides occurs at 10,110–10,260 cm\(^{-1}\) (975 to 989 nm). The second overtone of secondary amides is near 10,194 cm\(^{-1}\) (981 nm).


The second overtone of primary amides occurs at 10,110–10,260 cm\(^{-1}\) (975 to 989 nm). The second overtone of secondary amides is near 10,194 cm\(^{-1}\) (981 nm).

**8.5.2 AMIDES, COMBINATIONS**

In primary amides, a single combination band of symmetric and asymmetric NH stretching appears at 6805 cm\(^{-1}\) (1470 nm). Several bands near 5100 and 4925 cm\(^{-1}\) (1960 and 2030 nm) have been assigned to the combinations of NH stretch and amide II and III deformations (these mid-infrared bands are generally considered to be due to different types of coupling of the CNH deformation and
Amines and Amides

CN stretch). For example, a strong band at 5100 cm\(^{-1}\) (1960 nm) has been assigned to the combination of asymmetric NH stretching with amide II. Two weak bands at 4925 cm\(^{-1}\) (2030 nm) and 4975 cm\(^{-1}\) (2010 nm) have been attributed to the combination of asymmetric NH stretching with amide III and symmetric NH stretching with amide III, respectively.

The near-infrared spectrum of urea, a special case of primary amide, was described by Murray.\(^{20}\) Urea and thiourea were also discussed by Bala and Ghosh.\(^{21}\) Table 8.4 provides a summary of its overtone and combination peaks. The fundamental bands listed in the table provide background information to help explain the combinations.

For secondary amides, the combination bands in the range of 4950–5000 cm\(^{-1}\) (2000–2020 nm) and 4695–4740 cm\(^{-1}\) (2110–2130 nm) were assigned to the NH stretch with amide II and NH stretch with amide III, respectively.\(^{22}\) An additional band at 4630 cm\(^{-1}\) (2160 nm) was attributed to the combination of the first overtone of C=O with amide III (\(2\nu_{\text{C=O}} + \text{amide III}\)).\(^{23}\)

The main combination bands of secondary amides are summarized in Table 8.5. These bands are important in the analysis of proteins. As explained by Murray in his chapter on spectral comparisons,\(^{24}\) two of the combination bands of proteins lie on either side of the OH combination band of carbohydrates. Therefore, the shape of the spectral region near 4760 cm\(^{-1}\) (2100 nm) is

---

**TABLE 8.4**

**Summary of Urea Absorptions**

<table>
<thead>
<tr>
<th>Mid-Infrared fundamental bands</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH asymmetrical stretch</td>
<td>3400</td>
<td>2941</td>
</tr>
<tr>
<td>NH symmetrical stretch</td>
<td>3300</td>
<td>3030</td>
</tr>
<tr>
<td>C=O stretch (amide I)</td>
<td>1610</td>
<td>6211</td>
</tr>
<tr>
<td>NH(_2) deformation coupled with C-N stretch (amide II)</td>
<td>1630</td>
<td>6135</td>
</tr>
<tr>
<td>C-N stretch coupled with NH(_2) deform (amide III)</td>
<td>1467</td>
<td>6817</td>
</tr>
<tr>
<td>NH(_2) wagging</td>
<td>1150</td>
<td>8696</td>
</tr>
</tbody>
</table>

**Near-Infrared bands**

| 1st overtone NH asymmetrical stretch | 6803 | 1470 |
| 1st overtone NH symmetrical stretch | 6736 | 1485 |
| NH asymmetrical + NH symmetrical stretch | 6666 | 1500 |
| Asymmetrical NH stretch + amide II | 5025 | 1990 |
| Symmetrical NH stretch + amide II | 4902 | 2040 |
| Asymmetrical NH stretch + amide III | 4808 | 2080 |
| \(2 \times \text{amide I} + \text{amide III}\) | 4687 | 2180 |
| Asymmetrical NH stretch + NH\(_2\) rocking | 4505 | 2220 |

**TABLE 8.5**

**Summary of Secondary Amide Bands in Protein**

<table>
<thead>
<tr>
<th>Band Assignment</th>
<th>Wavenumber</th>
<th>Wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st overtone NH</td>
<td>6250–6540</td>
<td>1530–1600</td>
</tr>
<tr>
<td>NH stretch + amide II</td>
<td>4850</td>
<td>2060</td>
</tr>
<tr>
<td>(2 \times \text{C=O (amide I) + amide III})</td>
<td>4590</td>
<td>2180</td>
</tr>
</tbody>
</table>
indicative of the relative amounts of protein and carbohydrate in food and agricultural products. Secondary amide peaks are also important in the analysis of nylon and many pharmaceuticals.

Wu and Siesler have assigned additional secondary amide bands in their study of the aliphatic polymer polyamide 11 (PA11). Using deuteration, variable temperature, and polarization measurements, the assignments listed in Table 8.6 were made.

The tertiary amides lack the NH absorptions observed in the primary and secondary amides. A band at 4675 cm\(^{-1}\) (2139 nm) for \(N, N\)-dimethylformamide, at 4650 cm\(^{-1}\) (2151 nm) for \(N, N\)-diethylacetamide, and at 4630 cm\(^{-1}\) (2160 nm) for \(N, N\)-dimethylbenzamide corresponds to the combination band of \(2\nu_{C=O} + \text{amide III}\).

### 8.6 AMIDES, CYCLIC (LACTAMS)

Near-infrared spectra of lactams primarily show bands attributable to nonhydrogen-bonded amides. This is in contrast to linear secondary amides, which do show hydrogen-bonded peaks. The near-infrared region provides a means of distinguishing \(cis\) (cyclic) and \(trans\) (linear) amides, especially for hydrogen-bonding studies. Table 8.7 summarizes the band assignments for the unassociated lactam amide bands.

**TABLE 8.6**

Secondary Amide Bands in Polyamide 11

<table>
<thead>
<tr>
<th>Band Assignment</th>
<th>Wavenumber</th>
<th>Wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st overtone nonbonded NH</td>
<td>6760</td>
<td>1480</td>
</tr>
<tr>
<td>1st overtone bonded NH, disordered phase</td>
<td>6600</td>
<td>1515</td>
</tr>
<tr>
<td>1st overtone bonded NH, ordered phase</td>
<td>6500</td>
<td>1538</td>
</tr>
<tr>
<td>Bonded NH + 2 × amide II</td>
<td>6368</td>
<td>1570</td>
</tr>
<tr>
<td>Amide I + 3 × amide II</td>
<td>6256</td>
<td>1598</td>
</tr>
<tr>
<td>4 × amide II</td>
<td>6180</td>
<td>1618</td>
</tr>
<tr>
<td>Bonded NH + amide I</td>
<td>4970</td>
<td>2012</td>
</tr>
<tr>
<td>Bonded NH + amide II</td>
<td>4870</td>
<td>2053</td>
</tr>
<tr>
<td>2 × amide II + amide I</td>
<td>4701</td>
<td>2127</td>
</tr>
<tr>
<td>Bonded NH + amide III</td>
<td>4586</td>
<td>2183</td>
</tr>
<tr>
<td>2 × amide I + amide III</td>
<td>4521</td>
<td>2212</td>
</tr>
</tbody>
</table>

*Note: See Table 8.4 for explanation of nomenclature.*

**TABLE 8.7**

Unassociated Amides Peaks for Gamma-Valerolactam in CCl\(_4\)

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH stretch + NH bending</td>
<td>4865</td>
<td>2055</td>
</tr>
<tr>
<td>NH stretch + amide II</td>
<td>4785</td>
<td>2090</td>
</tr>
<tr>
<td>NH stretch + amide III</td>
<td>4715</td>
<td>2120</td>
</tr>
<tr>
<td>2 × (C=O) (amide I) + amide III</td>
<td>4660</td>
<td>2145</td>
</tr>
</tbody>
</table>
Amines and Amides

REFERENCES

20. Murray, I., op. cit.
24. Murray, I., op. cit.
9 P-H and S-H

9.1 P-H

The first overtone of P-H stretching was found at 5288 cm\(^{-1}\) (1891 nm) in a number of organo-phosphorus compounds. It is slightly more intense than the S-H absorption, having a molar absorptivity of about 0.24 l/mol-cm. It is described as being more diffuse and less sharp, however.1

The POH group is observed in phosphorothioic acids. The absorption is significantly shifted relative to the hydroxyl in alcohols, as it is in mid-infrared. The near-infrared (NIR) peak appears at about 5241 cm\(^{-1}\) (1908 nm).

9.2 S-H

Goddu mentions a weak S-H first overtone band for benzenethiol and 1-butanethiol at 5076–5051 cm\(^{-1}\) (1970 to 1980 nm).2 He cites molar absorptivities of 0.081 and 0.044 l/mol-cm, respectively. This band is probably a nonbonded S-H. It is also weak in the mid-infrared, although strong in the Raman. Although a bonded S-H would be broader and placed at a lower wavenumber (higher wavelength), Williams has indicated that the S-H is not as amenable to hydrogen bonding as the O-H. Liquid thiols (mercaptans) have sharper peaks than liquid alcohols.3

The first overtone of the S-H group can be seen in Figure 9.1 as the weak peak near 5050 cm\(^{-1}\).

The phosphorus-thiol group (P-SH) shows a shift from the normal thiol overtone and gives rise to a weak doublet at 5076–5002 cm\(^{-1}\) (1970 and 1999 nm).4

![Figure 9.1](image_url)
REFERENCES

10 Carbohydrates

10.1 INTRODUCTION

Carbohydrates include saccharides and polysaccharides, or sugars and starches, and cellulotic or lignin type biomolecules. They consist mostly of aliphatic cyclic groups with attached OH groups and ether linkages. Lignin is representative of aromatic natural product compounds. Thus, the bands normally associated with these functional groups may be observed in the near-infrared (NIR) spectra of carbohydrate molecules.

Table 10.1 is a useful reference indicating the appearance of bands related to starches and sugars. Figure 10.1 shows two of these classic spectra, cornstarch and sucrose. Note the sharp nonbonded OH peak near 1430 nm and the lack of a water peak near 1940 nm in sucrose.

10.2 CELLULOSE AND CELLULOSIC COMPOUNDS

An excellent reference article for background reading is supplied by Blackwell. The article reviews the work in infrared and Raman spectroscopy of cellulosic materials up to 1977, including a detailed table giving calculated and observed band assignments for cellulose I. Table 10.2 shows observed band positions for cellulose I functional groups with corresponding first and second overtone positions between 996 nm and 2500 nm (9091 to 4000 cm\(^{-1}\)), and Figure 10.2 shows its spectrum. Bands thought to associate with fiber parameters, such as cellulose and lignin are presented in Table 10.3 and Table 10.4, respectively. Multiple quantitative calibrations have demonstrated that cellulose and lignin are determined using the regions from 4348 to 4237 cm\(^{-1}\) (2300 to 2360 nm) and 6042 to 5865 cm\(^{-1}\) (1655 to 1715 nm.)

Wingfield discussed the possibilities for NIR detection of cellulose in flour. He summarizes work up until the publication of his book and cites early workers in the field. Marton and Sparks have reported measurements of lignocellulose in the infrared region by using simple linear regression of lignin content vs. the absorbance ratio of 1510/1310 cm\(^{-1}\); these frequencies correspond to a ratio of second overtones occurring near 4529/3929 cm\(^{-1}\) (2208/2545 nm). Lignin exhibits the strong presence of many aromatic rings and associated functional groups (see Table 10.4).

Gould et al. reported using an infrared frequency shift of the 2900-cm\(^{-1}\) band (3448-nm), which would correspond to a frequency shift at a first overtone band near 5800 cm\(^{-1}\) (1724 nm). Mitchell and coworkers determined the acetyl content of cellulose acetate using NIR from 35 to 44.8% acetyl. The spectra were measured in 5-cm cells against a reference solution of pyrrole containing 5% carbon tetrachloride. The maximum absorbance at 6920 cm\(^{-1}\) (1445 nm) was plotted against percent acetyl to obtain a calibration line. A standard deviation of 0.22% was indicated by the NIR method. Near-infrared spectroscopy was evaluated for monitoring the acid-catalyzed hydrolysis (thinning) of starch (I) using a univariate calibration model based on the integrated area of the 4400-cm\(^{-1}\) (2272-nm) absorption band for carbohydrates.
TABLE 10.1
Bands Associated with Starches and Sugars as C–H- and O–H-Related Bands

<table>
<thead>
<tr>
<th>Functional Grouping</th>
<th>Nanometers</th>
<th>Wavenumbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–H stretching and C–C and C–O–C stretching combination</td>
<td>2500</td>
<td>4000</td>
</tr>
<tr>
<td>C–H stretching and CH₃ deformation combinations</td>
<td>2280–2330</td>
<td>4283–4386</td>
</tr>
<tr>
<td>O–H bending and C–O stretching combination. O–H/C–O</td>
<td>2100</td>
<td>4762</td>
</tr>
<tr>
<td>Polymeric (O–H and C–O)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O–H (2ν), O–H – O–H polymeric (.O–H)</td>
<td>1450</td>
<td>6897</td>
</tr>
<tr>
<td>3νO–H, saccharides</td>
<td>1009 and 972</td>
<td>9911 and 10,288 (doublet)</td>
</tr>
</tbody>
</table>

FIGURE 10.1 Corn starch (solid curve) and sucrose (dotted curve).

TABLE 10.2
Cellulose I Associated Bands

<table>
<thead>
<tr>
<th>Functional Grouping</th>
<th>Nanometers</th>
<th>Wavenumbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–H stretching and C–C and C–O–C stretching combination</td>
<td>2500</td>
<td>4000</td>
</tr>
<tr>
<td>C–H stretching and C–C stretching combination</td>
<td>2488</td>
<td>4019</td>
</tr>
<tr>
<td>3 × (C–H bending): C–H</td>
<td>2352</td>
<td>4252</td>
</tr>
<tr>
<td>C–H (2ν CH₃ symmetric stretching and δ CH₃) combination</td>
<td>2347</td>
<td>4261</td>
</tr>
<tr>
<td>C–H stretching and CH₃ deformation combination</td>
<td>2280–2330</td>
<td>4283–4386</td>
</tr>
<tr>
<td>O–H/C–H Cellulose</td>
<td>2270</td>
<td>4405</td>
</tr>
<tr>
<td>O–H polymeric O–H (2ν)</td>
<td>2090</td>
<td>4785</td>
</tr>
<tr>
<td>O–H stretching and C–O stretching (3ν) combination</td>
<td>1820</td>
<td>5495</td>
</tr>
<tr>
<td>C–H Methylene (2νC–H)</td>
<td>1780</td>
<td>5618</td>
</tr>
<tr>
<td>O–H Polymeric (2νO–H)</td>
<td>1450</td>
<td>6897</td>
</tr>
<tr>
<td>O–H (3ν)</td>
<td>996</td>
<td>10,040</td>
</tr>
</tbody>
</table>
FIGURE 10.2 Cellulose.

TABLE 10.3
Bands Normally Associated with “Fiber” as Cellulosics

<table>
<thead>
<tr>
<th>Functional Grouping</th>
<th>Nanometers</th>
<th>Wavenumbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–H stretching and C–C stretching combination</td>
<td>2488</td>
<td>4019</td>
</tr>
<tr>
<td>C–H bending</td>
<td>2352</td>
<td>4252</td>
</tr>
<tr>
<td>C–H (2νCH₂ symmetric stretching and δ CH₂) combination</td>
<td>2347</td>
<td>4261</td>
</tr>
<tr>
<td>C–H stretching plus CH₂ deformation combination</td>
<td>2335</td>
<td>4283</td>
</tr>
<tr>
<td>O–H stretching plus 2 × C–O stretching combination</td>
<td>1820</td>
<td>5495</td>
</tr>
<tr>
<td>CH₂ stretching (2ν)</td>
<td>1780</td>
<td>5618</td>
</tr>
<tr>
<td>O–H (3ν) (–CH₂–OH)</td>
<td>996</td>
<td>10,040</td>
</tr>
</tbody>
</table>

TABLE 10.4
Bands Normally Associated with “Fiber” as Lignins

<table>
<thead>
<tr>
<th>Functional Grouping</th>
<th>Nanometers</th>
<th>Wavenumbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCα + CHν (11 + 12), aromatic ring band assignment</td>
<td>2540</td>
<td>3937 (3935)</td>
</tr>
<tr>
<td>C–H stretching and C=O combination</td>
<td>2200</td>
<td>4545</td>
</tr>
<tr>
<td>C–H (2ν), ArC–H: C–H aromatic associated C–H</td>
<td>1685</td>
<td>5935</td>
</tr>
<tr>
<td>C–H (2νCH₂ and δ CH₂) combination: C–H methylene</td>
<td>1410</td>
<td>7092</td>
</tr>
<tr>
<td>C–H, associated with linear aliphatic R(CH₃)ₙR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C–H combination, aromatic associated C–H</td>
<td>1417</td>
<td>7057</td>
</tr>
<tr>
<td>C–H (3ν), .HC=CH</td>
<td>1170</td>
<td>8547</td>
</tr>
<tr>
<td>C–H (4ν), aromatic associated C–H</td>
<td>876</td>
<td>11,655</td>
</tr>
</tbody>
</table>
REFERENCES

11 Amino Acids, Peptides, and Proteins

11.1 PROTEINS

Protein is measured in the near-infrared (NIR) region as its associated functional groups, such as amides and various C–H functional groups. For example, key band locations associated with proteins are found at 10,277 to 9804 cm\(^{-1}\) (973 to 1020 nm) as N–H stretch second overtone; 6667 to 6536 cm\(^{-1}\) (1500 to 1530 nm) as N–H stretching first overtone; and 4878 to 4854 cm\(^{-1}\) (2050 to 2060 nm) representing N–H-stretching combinations. The 4613- to 4587-cm\(^{-1}\) (2168 to 2180-nm) region is associated with the N–H bend second overtone and C=O stretch/N–H in-plane bending/C–N stretch combination bands. See Chapter 8 for a more complete description of amide bands.

Hermans and Scheraga\(^1\) made measurements of the backbone peptide hydrogen bond system (NH group) using NIR measurements in the extended spectral region from 14,286 to 2,857 cm\(^{-1}\) (700–3500 nm). The authors describe the use of NIR to distinguish between hydrogen-bonded and non-hydrogen-bonded N–H and O–H groups. Molecules examined include methanol, aniline, and poly-\(\gamma\)-benzyl-L-glutamate.

Elliott and Ambrose\(^2\) identified absorption bands for polypeptides and proteins at approximately 3505 cm\(^{-1}\) (2853 nm) as N–H-associated stretching bands and at 4825 cm\(^{-1}\) (2073 nm) in the overtone region. The main result of their work was to demonstrate that a band at 4840 cm\(^{-1}\) (2066 nm) is useful for distinguishing the presence of extended vs. folded configurations for polypeptides and proteins even in the presence of liquid-phase water. The band near 4824 cm\(^{-1}\) (2073 nm) was classified earlier by Glatt and Ellis\(^3\) on work in nylon as a combination band of the N–H deformation and stretching modes.

Hecht and Wood\(^4\) described in a detailed study the band assignments for peptides. The authors identified the bands for a porcupine quill spectrum as shown in Table 11.1.

A summary of all bands thought to be associated with protein as amides is presented in Table 11.2. Multiple quantitative calibrations for protein in the agricultural literature demonstrate the area from 4655 to 4545 cm\(^{-1}\) (2148 to 2200 nm) as used for protein determination.\(^5\)

Fraser and MacRae\(^6\) have reported important absorption bands for natural product proteins and nylon polyamide at 4870 cm\(^{-1}\) (2188 nm) resulting from a combination of the peptide absorptions at 3305 cm\(^{-1}\) (3026 nm) and 1540 cm\(^{-1}\) (6494 nm). For feather shafts, the authors report absorption bands at 4970 cm\(^{-1}\) (2012 nm) and 5040 cm\(^{-1}\) (1984 nm). A shoulder at 5040 cm\(^{-1}\) (1984 nm) was reported as resulting from side chain amide groups. For beta-keratin, the paper reports important absorption bands at 4600 cm\(^{-1}\) (2174 nm), 4850 cm\(^{-1}\) (2062 nm), and 4970 cm\(^{-1}\) (2012 nm). The authors were interested in studying the amorphous components of naturally occurring protein structures.

11.2 PROTEIN STRUCTURE

The most pronounced changes for the thermal unfolding of RNase A are observed from 4820 to 4940 cm\(^{-1}\). The strong N–H combination band found at 4867 cm\(^{-1}\) in the spectrum of native RNase A shifts to 4878 cm\(^{-1}\) upon thermal unfolding. The thermal unfolding of RNase A begins with some changes in \(\beta\)-sheet structure, followed by the loss of \(\alpha\)-helical structures, and then ending with the unfolding of the remaining \(\beta\)-sheets.\(^7\) Fourier transform near-infrared (FT-NIR) spectra have been measured for
### TABLE 11.1
Band Assignments for Peptide Groups as Delineated by K.T. Hecht and D.L. Wood

<table>
<thead>
<tr>
<th>Reported Band Assignments</th>
<th>Wavenumber</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–H stretch + CH deformation</td>
<td>3950–4400</td>
<td>2532–2270</td>
</tr>
<tr>
<td>2 × stretch C=O + peptide group mode</td>
<td>4590</td>
<td>2180</td>
</tr>
<tr>
<td>N–H stretch + peptide group mode</td>
<td>4850</td>
<td>2060</td>
</tr>
<tr>
<td>OH stretch + OH deformation of water</td>
<td>5135</td>
<td>1947</td>
</tr>
<tr>
<td>2 × C–H stretch</td>
<td>5700–5850</td>
<td>1750–1710</td>
</tr>
<tr>
<td>2 × NH stretch</td>
<td>6500</td>
<td>1540</td>
</tr>
<tr>
<td>2 × OH stretch + deformation of water</td>
<td>6900</td>
<td>1450</td>
</tr>
<tr>
<td>3 × C–H stretch</td>
<td>8100</td>
<td>1235</td>
</tr>
</tbody>
</table>

### TABLE 11.2
Absorption Bands Associated with “Proteins” as Amides

<table>
<thead>
<tr>
<th>Functional Grouping</th>
<th>Nanometers</th>
<th>Wavenumbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>N–H/C–N/N–H [bonded NH stretching and amide III (C–N stretching/N–H in-plane bending) combination] from polyamide 11</td>
<td>2183</td>
<td>4586</td>
</tr>
<tr>
<td>N–H (3δ)</td>
<td>2180</td>
<td>4587</td>
</tr>
<tr>
<td>N–H/C–N/C=O [2 × amide I (2νs C=O stretching) and amide III deformation (C–N stretching/N–H in-plane bending) combination] for urea</td>
<td>2180</td>
<td>4687</td>
</tr>
<tr>
<td>N–H/C–N/C=O [2 × amide I (2νs C=O stretching) and amide III deformation (C–N stretching/N–H in-plane bending) combination] for secondary amides in proteins</td>
<td>2180</td>
<td>4590</td>
</tr>
<tr>
<td>N–H/C–N [νs N–H asymmetric and amide III deformation (C–N stretching/N–H in-plane bending) combination] for urea</td>
<td>2080</td>
<td>4808</td>
</tr>
<tr>
<td>N–H [νN–H and amide II deformation (N–H in-plane bending) combination] for secondary amides in native RNase A</td>
<td>2075</td>
<td>4820</td>
</tr>
<tr>
<td>N–H (3δ) and N–H stretching combination</td>
<td>2060</td>
<td>4854</td>
</tr>
<tr>
<td>N–H [νN–H and amide II deformation (N–H in-plane bending) combination] for secondary amides in proteins</td>
<td>2060</td>
<td>4850</td>
</tr>
<tr>
<td>CONH₂ combination of amide A and amide II</td>
<td>2060</td>
<td>4855</td>
</tr>
<tr>
<td>N–H stretching and C=O stretching (amide I) combination</td>
<td>2055</td>
<td>4866</td>
</tr>
<tr>
<td>N–H [νN–H and δN–H combination] for gamma-valerolactam</td>
<td>2055</td>
<td>4865</td>
</tr>
<tr>
<td>N–H combination band found in the spectrum of native RNase A (C=O amide I band)</td>
<td>2055</td>
<td>4867</td>
</tr>
<tr>
<td>CONH₂ specifically due to peptide β-sheet structures</td>
<td>2055</td>
<td>4865</td>
</tr>
<tr>
<td>N–H stretching and C=O stretching (amide I) combination in the spectrum of native RNase A</td>
<td>2055</td>
<td>4867</td>
</tr>
<tr>
<td>N–H from CONH₂ as thermal unfolding of RNase A protein in aqueous solution (assigned to an N–H combination band)</td>
<td>2055–2050</td>
<td>4867–4878</td>
</tr>
<tr>
<td>N–H in-plane bend and C–N stretching and N–H in-plane bend combination</td>
<td>2050</td>
<td>4878</td>
</tr>
<tr>
<td>N–H native RNase A combination band at 4867 cm⁻¹ shifting due to thermal unfolding (C=O amide I band)</td>
<td>2050</td>
<td>4878</td>
</tr>
<tr>
<td>N–H stretching and C=O stretching (amide I) combination band observed in the thermal unfolding observed in native RNase A</td>
<td>2050</td>
<td>4878</td>
</tr>
<tr>
<td>N–H [νN–H symmetric and amide II deformation (N–H in-plane bending) combination] for primary amides</td>
<td>2040</td>
<td>4902</td>
</tr>
<tr>
<td>C=O (3ν), C=ONH₂</td>
<td>2030</td>
<td>4926</td>
</tr>
</tbody>
</table>
various polypeptides and proteins with different secondary structures in order to identify an NIR marker band for the protein and polypeptide structures. Comparison between FT-NIR and FT–mid-infrared spectra has shown a correlation between the frequency of a band near 4855 cm\(^{-1}\), assignable to a combination of amide A and amide II, and that of a mid-infrared band near 3300 cm\(^{-1}\), assigned to amide A (N\(\overset{-}{\text{H}}\) stretch).\(^8\) The NIR spectra of various proteins (bovine serum albumin, lysozyme, ovalbumin, \(\gamma\)-globulin, \(\beta\)-lactoglobulin, myoglobin, cytochrome c) have been investigated for potential measurement of protein secondary structure. The spectra of proteins in aqueous solutions and as freeze-dried solids indicated \(\alpha\)-helix information present at 4090, 4365–4370, 4615, and 5755 cm\(^{-1}\); and \(\beta\)-sheet information at 4060, 4405, 4525–4540, 4865, and 5915–5925 cm\(^{-1}\).\(^9\)

Ovalbumin (OV A) has been studied in acidified, aqueous solutions using two-dimensional (2-D) FT-NIR correlation spectroscopy. This technique demonstrates a significant change in bands when the molecule pH moves from 5.4 to 3.6. A band near 4265 cm\(^{-1}\) assigned to a symmetric methylene (CH\(_2\))-stretching mode and a CH\(_2\)-bending mode of side chains observed at pH 5.4 disappears completely in the synchronous spectrum at pH 3.6. A band near 4600 cm\(^{-1}\) assigned to a combination of amide B (a Fermi resonance band relating to the first overtone of the carbonyl and the N–H stretch) and amide II shifts downward with significant broadening between pH 3.0 and 2.4. A broad band at around 6950 cm\(^{-1}\) that was assigned to free water and bound water with weak hydrogen bonds becomes very weak in the synchronous spectrum at pH 2.6, while broad auto peaks around 6450 cm\(^{-1}\) suddenly appear that are due to bound water with several hydrogen bonds and the first overtone of an NH-stretching mode of the amide groups of OV A.\(^{10}\) FT-NIR spectra have been measured for several globular proteins, and a band near 4525 cm\(^{-1}\) seems to be highly associated with \(\beta\)-sheet structure. Low-wavenumber NIR bands from the 4500–4000-cm\(^{-1}\) region were considered to reflect the amino acid composition of proteins.\(^{11}\)

REFERENCES

12 Synthetic Polymers and Rubbers*

12.1 INTRODUCTION

Near-infrared (NIR) is routinely used to qualify monomers prior to polymerization reactions. It is used to measure the kinetics of polymer onset and can be used to detect end-point completion and initiator compound levels in polymerization reactions. NIR spectroscopy can also be used to sort polymers and to control the quality of incoming raw monomers and finished polymeric materials. Molecular spectroscopy using NIR and IR measurement techniques is often used for competitive analysis and to determine thermal or photo-induced oxidation or degradation reactions in polymers. In general, NIR spectroscopy is valuable for polymer identification, characterization, and quantitation. NIR spectroscopy can be completed for in situ process applications where no sample preparation is a requirement, and where rugged optical systems are a necessity. Some of the earliest work in applying IR and NIR spectroscopy to polymer characterization is found in References 1 to 11.

12.2 INTERPRETIVE SPECTROSCOPY OF ORGANIC COMPOUND SPECTRA FOR POLYMERS AND RUBBERS IN THE NIR REGION

Polymers and rubbers exhibit characteristic band positions that will vary depending upon the molecular structure and the associated or attached chemical groups. Table 12.1 briefly demonstrates the positions for the major chemical groups encountered in analysis of polymer and rubber materials. The accompanying text describes the individual molecular vibrations and band assignments in much greater detail.

12.3 POLYMERS

Polymers are usually large molecules consisting of repeating units or monomers. Natural polymers exist, such as starches or polysaccharides. Synthetic polymers are commonly termed plastics and are used for many commonly used materials and products. Polymers vary in molecular formula and molecular weight due to variation in the number or repeating units. Polymer backbone structures often have attached molecular groups. The molecular arrangement of these groups determines the stereo-chemical configuration for any given polymer. If all the attached groups are in the identical position along the polymer backbone chain, the polymer is in an isotactic configuration. If the attached groups alternate in their attached positions with a regular pattern, the syndiotactic configuration is ascribed. When attached groups are randomly attached to the polymer backbone, the polymer is said to have an atactic configuration. The isotactic configuration represents the most crystalline (rigid) of the configuration types.

Copolymers involve the use of two or more monomer types into a single backbone structure to achieve specific material performance properties. Structures are classified as alternating

### TABLE 12.1
C-H, N-H, and O-H Stretch Absorption Bands for Specific Long-Wavelength NIR (1100–2500 nm) Functional Groups (1st (2ν) through 4th (4ν)) C-H-Stretching Overtones

<table>
<thead>
<tr>
<th>Structure</th>
<th>Bond Vibration</th>
<th>Location of (2ν)</th>
<th>Location of (3ν)</th>
<th>Location of (4ν)</th>
<th>Location of (5ν)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1st Overtone</td>
<td>2nd Overtone</td>
<td>3rd Overtone</td>
<td>4th Overtone</td>
</tr>
<tr>
<td>R-OH (Alcohols)</td>
<td>O-H stretching</td>
<td>6981 cm⁻¹</td>
<td>10,471 cm⁻¹</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1410–1455 nm</td>
<td>940–970 nm</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>ArOH (Phenols)</td>
<td>O-H stretching</td>
<td>6918 cm⁻¹</td>
<td>10,417 cm⁻¹</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1421–1470 nm</td>
<td>940–980 nm</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Starch</td>
<td>O-H stretching</td>
<td>6892 cm⁻¹</td>
<td>10,341 cm⁻¹</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1451 nm</td>
<td>967 nm</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Urea (Symmetric N-H stretching)</td>
<td></td>
<td>6849 cm⁻¹</td>
<td>10,173 cm⁻¹</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1460 nm</td>
<td>973–993 nm</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>HOH (Water)</td>
<td>O-H stretching</td>
<td>6838 cm⁻¹</td>
<td>10,417 cm⁻¹</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1440–1485 nm</td>
<td>960 nm</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>CONHR (Secondary amides)</td>
<td>N-H stretching</td>
<td>6793 cm⁻¹</td>
<td>10,194 cm⁻¹</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1472 nm</td>
<td>981 nm</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>CONH₂ (Primary amides)</td>
<td>N-H stretching</td>
<td>6787 cm⁻¹</td>
<td>10,183 cm⁻¹</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1463–1484 nm</td>
<td>975–989 nm</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Cellulose</td>
<td>O-H stretching</td>
<td>6711 cm⁻¹</td>
<td>10,070 cm⁻¹</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1490 nm</td>
<td>993 nm</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>ArNH₂ (Aromatic amines)</td>
<td>N-H stretching</td>
<td>6698 cm⁻¹</td>
<td>10,050 cm⁻¹</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1493 nm</td>
<td>995 nm</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>NH (Amines, general)</td>
<td>N-H stretching</td>
<td>6667 cm⁻¹</td>
<td>10,000 cm⁻¹</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1500 nm</td>
<td>1000 nm</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Protein</td>
<td>N-H stretching</td>
<td>6618 cm⁻¹</td>
<td>9930 cm⁻¹</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1511 nm</td>
<td>1007 nm</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>ArCH (Aromatics)</td>
<td>C-H stretching</td>
<td>5945 cm⁻¹</td>
<td>8749 cm⁻¹</td>
<td>11,429 cm⁻¹</td>
<td>13,986 cm⁻¹</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1680–1684 nm</td>
<td>1143 nm</td>
<td>875 nm</td>
<td>715 nm</td>
</tr>
<tr>
<td>CH₂−CH₂ (Methylene)</td>
<td>C-H stretching</td>
<td>5792 cm⁻¹</td>
<td>8251 cm⁻¹</td>
<td>10,770 cm⁻¹</td>
<td>13,115 cm⁻¹</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1726–1727 nm</td>
<td>1212 nm</td>
<td>927–930 nm</td>
<td>761–764 nm</td>
</tr>
<tr>
<td>CH₃ (Methyl)</td>
<td>C-H stretching</td>
<td>5706 cm⁻¹</td>
<td>8386 cm⁻¹</td>
<td>10,953 cm⁻¹</td>
<td>13,396 cm⁻¹</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1743–1762 nm</td>
<td>1191–1194 nm</td>
<td>911–915 nm</td>
<td>745–748 nm</td>
</tr>
<tr>
<td>CH₃ (Methyl)</td>
<td>C-H combination</td>
<td>4914 cm⁻¹</td>
<td>7369 cm⁻¹</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2020–2050 nm</td>
<td>1347–1367 nm</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>&gt;C=O (Carbonyl)</td>
<td>&gt;C=O stretching</td>
<td>3431 cm⁻¹</td>
<td>5175 cm⁻¹</td>
<td>6944 cm⁻¹</td>
<td>8658 cm⁻¹</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2915 nm</td>
<td>1920–1945 nm</td>
<td>1420–1460 nm</td>
<td>1140–1170 nm</td>
</tr>
</tbody>
</table>


---

**FIGURE 12.1** Polypropylene is a polyolefin comprised of repeating olefin monomer units.

![Polypropylene](image_url)
Polymerization involves the reaction of the monomer building blocks into polymers. The polymerization reaction types involve addition reactions and condensation reactions. Addition reactions typically involve the use of ethene to form polyethylene and polyethylene. Condensation reactions typically involve different reaction products reacting to form a heteropolymer and a small molecular by-product. The reaction of 1,6-diaminobutane and hexanedioc acid to form nylon and water is a classic example. Polymers made from one monomer type are termed homopolymers, and those formed with two different monomers are referred to as copolymers.

A few example polymers are shown in the following figures (Figure 12.1, Figure 12.2, Figure 12.3, Figure 12.4, Figure 12.5, Figure 12.6).

Typical polymer spectra exhibit similar NIR bands and positions, which are represented in Table 12.2.

12.4 RUBBERS

Rubber or elastomer is a natural or synthetic material having the ability to undergo deformation under the influence of an applied force and regain its original shape once the applied force is removed. Natural rubbers are polymeric materials originally obtained from the rubber tree (Hevea brasiliensis). The sap of this tree is a latex material that is processed by coagulation and drying the sap, and then vulcanizing and adding filler compounds. The basic natural rubber compound is isoprene, which contains the repeating unit of \( \text{CH}_2\text{C(CH}_3\text{)}\text{CHCH}_2\text{.} \) Synthetic rubbers exist such as nitriles, butadienes, neoprene, butyl rubbers, polysulfide rubbers, PVC, and silicone rubbers, whose structures and NIR spectra are shown in Figure 12.7, Figure 12.8, Figure 12.9, and Figure 12.10.

---

FIGURE 12.2B An NIR wavenumber spectrum of atactic poly(propylene) at low resolution (32 cm$^{-1}$).

![NIR wavenumber spectrum of atactic poly(propylene) at low resolution (32 cm$^{-1}$).](image)

FIGURE 12.3 Structure of styrene monomer units found in polystyrene.

![Structure of styrene monomer units found in polystyrene.](image)

FIGURE 12.4 NIR spectrum of crystalline poly(styrene) at 16-cm$^{-1}$ resolution.

![NIR spectrum of crystalline poly(styrene) at 16-cm$^{-1}$ resolution.](image)
Synthetic Polymers and Rubbers

FIGURE 12.5 Two examples of water-soluble polymers as polyacrylates.

\[
\begin{align*}
\text{Polyacrylic acid} & \quad \text{Polymethacrylic acid} \\
\ce{CH2-CH-COOH^\text{n}} & \quad \ce{CH2-C-COOH^\text{n}}
\end{align*}
\]

FIGURE 12.6A NIR wavelength spectrum of poly(acrylic acid) at 32-cm$^{-1}$ resolution.

FIGURE 12.6B NIR wavenumber spectrum of poly(acrylic acid) at 32-cm$^{-1}$ resolution.
### TABLE 12.2
Spectral Correlation Chart for Example Polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Band Locations</th>
<th>Band Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(propylene)</td>
<td>9930 cm⁻¹ (1192 nm)</td>
<td>Asymmetric methyl (C=H) stretch (3ν) 2nd overtone</td>
</tr>
<tr>
<td></td>
<td>8197 cm⁻¹ (1220 nm)</td>
<td>Asymmetric methylene (C=H) stretch (3ν) 2nd overtone</td>
</tr>
<tr>
<td></td>
<td>7174 cm⁻¹ (1394 nm)</td>
<td>Methyl and methylene (C=H) combination</td>
</tr>
<tr>
<td></td>
<td>5882 cm⁻¹ (1700 nm)</td>
<td>Asymmetric methyl (C=H) stretch (2ν) 1st overtone</td>
</tr>
<tr>
<td></td>
<td>5794 cm⁻¹ (1726 nm)</td>
<td>Asymmetric methylene (C=H) stretch (2ν) 1st overtone</td>
</tr>
<tr>
<td></td>
<td>5495 cm⁻¹ (1820 nm)</td>
<td>Symmetric methyl (C=H) stretch (2ν) 1st overtone</td>
</tr>
<tr>
<td></td>
<td>4305 cm⁻¹ (2323 nm)</td>
<td>C=H bend (3δ) 2nd overtone</td>
</tr>
<tr>
<td></td>
<td>4196 cm⁻¹ (2383 nm)</td>
<td>C=H stretch and C=C stretching combination</td>
</tr>
<tr>
<td></td>
<td>4075 cm⁻¹ (2454 nm)</td>
<td>C=H combination band</td>
</tr>
<tr>
<td>Poly(styrene)</td>
<td>8757 cm⁻¹ (1142 nm)</td>
<td>Aromatic (C=H) stretch (3ν) 2nd overtone</td>
</tr>
<tr>
<td></td>
<td>5938 cm⁻¹ (1684 nm)</td>
<td>Aromatic (C=H) stretch (2ν) 1st overtone</td>
</tr>
<tr>
<td>Poly(acrylic acid)</td>
<td>8439 cm⁻¹ (1185 nm)</td>
<td>Asymmetric methylene (C=H) stretch (3ν) 2nd overtone</td>
</tr>
<tr>
<td></td>
<td>7003 cm⁻¹ (1428 nm)</td>
<td>O=H stretch (2ν) 1st overtone</td>
</tr>
<tr>
<td></td>
<td>5900 cm⁻¹ (1695 nm)</td>
<td>Asymmetric methyl (C=H) stretch (2ν) 1st overtone</td>
</tr>
<tr>
<td></td>
<td>5764 cm⁻¹ (1735 nm)</td>
<td>Asymmetric methylene (C=H) stretch (2ν) 1st overtone</td>
</tr>
<tr>
<td></td>
<td>5198 cm⁻¹ (1924 nm)</td>
<td>O=H stretch (2ν) 1st overtone + C=O stretch (2ν) 2nd overtone + O=H stretch/HOH deformation combination + O=H bend (3δ) 2nd overtone</td>
</tr>
<tr>
<td></td>
<td>4653 cm⁻¹ (2149 nm)</td>
<td>C=H stretch/C=O stretch combination + symmetric C=H deformation</td>
</tr>
<tr>
<td></td>
<td>4374 cm⁻¹ (2286 nm)</td>
<td>C=H stretch + CH2 deformation + C=H bend (3δ) 2nd overtone</td>
</tr>
<tr>
<td></td>
<td>4018 cm⁻¹ (2489 nm)</td>
<td>C=H stretch + C=C stretch + C=O=C stretch comb</td>
</tr>
</tbody>
</table>

**FIGURE 12.7** Typical repeating units found in natural rubbers (trans- (left) and cis- (right) forms).
FIGURE 12.8A NIR wavelength spectrum of styrene-isoprene-styrene at 32-cm$^{-1}$ resolution.

FIGURE 12.8B NIR wavenumber spectrum of styrene-isoprene-styrene at (32-cm$^{-1}$) resolution.

FIGURE 12.9 Silicone rubbers (polysiloxane). Note: The alkyl group is often substituted with a variety of different groups.
FIGURE 12.10A NIR wavelength spectrum of silicone (DMS) at low (32-cm\(^{-1}\)) resolution.

FIGURE 12.10B NIR wavenumber spectrum of silicone (DMS) at low (32-cm\(^{-1}\)) resolution.
Typical rubber spectra exhibit similar NIR bands and positions, which are represented in Table 12.3.

### Table 12.3
Spectral Correlation Charts for Model Rubber Compounds

<table>
<thead>
<tr>
<th>Rubber</th>
<th>Band Location</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene-isoprene-styrene</td>
<td>8368 cm⁻¹ (1195 nm)</td>
<td>Methyl (C=H) stretch (3ν) 2nd overtone</td>
</tr>
<tr>
<td></td>
<td>7143 cm⁻¹ (1400 nm)</td>
<td>C=H stretch mode combination</td>
</tr>
<tr>
<td></td>
<td>5817 cm⁻¹ (1719 nm)</td>
<td>Asymmetric methylene (C=H) stretch (2ν) 1st overtone + aromatic C=H stretch (2ν) 1st overtone</td>
</tr>
<tr>
<td></td>
<td>4606 cm⁻¹ (2171 nm)</td>
<td>C=H bend (3ν) 2nd overtone</td>
</tr>
<tr>
<td></td>
<td>4365 cm⁻¹ (2291 nm)</td>
<td>C=H stretch + CH₂ deformation combination</td>
</tr>
<tr>
<td></td>
<td>4281 cm⁻¹ (2336 nm)</td>
<td>C=H stretch + CH₂ deformation combination</td>
</tr>
<tr>
<td></td>
<td>4049 cm⁻¹ (2470 nm)</td>
<td>C=H stretch + C=C stretch + C=O=C stretch combination</td>
</tr>
<tr>
<td>Silicone (dimethyl siloxane)</td>
<td>6887 cm⁻¹ (1452 nm)</td>
<td>Si=OH stretch (2ν) 1st overtone</td>
</tr>
<tr>
<td></td>
<td>5721 cm⁻¹ (1748 nm)</td>
<td>Methyl (C=H) stretch (2ν) 1st overtone</td>
</tr>
<tr>
<td></td>
<td>5173 cm⁻¹ (1933 nm)</td>
<td>Si=O=H stretch + Si=O=Si deformation combination</td>
</tr>
<tr>
<td></td>
<td>4357 cm⁻¹ (2295 nm)</td>
<td>C=H bend (3ν) 2nd overtone</td>
</tr>
</tbody>
</table>

**REFERENCES**

History of Near-Infrared (NIR) Applications

13.1 HISTORY OF NIR FOR INDUSTRIAL CHEMICALS

The application of NIR spectroscopy to the study of basic chemicals began in the 1800s. Following Herschel’s discovery of the phenomenon of radiation beyond the visible region, Abney and Festing recorded spectra of organic compounds photographically in 1881 and noted that they were related to the presence of hydrogen atoms. In 1896, Donath measured some organic compounds. In 1899–1900, Luigi Puccianti at the University of Pisa used a single quartz prism to study 15 hydrocarbon compounds. In 1904–1905, William W. Coblentz, working at the Carnegie Institute in Washington, D.C., measured the spectra of a number of compounds including benzene and chloroform from 800–2800 nm using a quartz prism and radiometer measured with the aid of a telescope. In 1922, Joseph W. Ellis at the University of California developed a recording spectrograph, measured a large number of organic compounds, and made many fundamental band assignments. Other early work on specific chemicals included that done at the U.S. Department of Agriculture by Liddel and Wulf, and at the U.S. Bureau of Standards by Rose, both in the 1930s.

In the 1940s, advances in instrumentation and the availability of commercial NIR instruments helped to bring about applications in the chemical and polymer industries. In 1949, Hibbard and Cleaves at the Lewis Flight Propulsion Laboratory in Cleveland, OH, studied hydrocarbon absorptions with the goal of analyzing octane and cetane numbers in reciprocating engine fuels, analyzing lubricating oils, and determining the structure of polymers. In the late 1940s and early 1950s, Lauer and Rosenbaum of Sun Oil also worked with hydrocarbons in the second overtone region. They mention studying natural and synthetic plastics including oriented nylon, polyvinyl chloride, and other polymers.

At about 1951, both Wilbur Kaye at Tennessee Eastman and Harry Willis in the Plastics Division of ICI in the U.K. began exploring NIR. Wilbur Kaye modified a Beckman DU UV instrument and worked on the development of the Beckman DK for NIR. Kaye thoroughly discussed the spectra of several compounds, including bromoform, chloroform, methylene chloride, benzene, methanol, and m-toluidine. He cited potential application of the spectral region to the analysis of mixtures of organic compounds, including water in hydrocarbons and other solvents, alcohols in hydrocarbons, acids, amines, benzene, and olefins in hydrocarbons.

Harry Willis initially designed and built an instrument with a small CsI prism. He worked with copolymer analyses, using thicker sheets of polymer than was possible with mid-infrared. Measurements were made quickly and directly. He was able to estimate monomer content, determine molecular weight by end-group analysis, and measure copolymers such as butadiene/styrene.

Two other industrial chemists who worked with developing NIR applications in the 1950s were Robert Goddu of Hercules Powder Company (now Hercules Incorporated) and Kermit Whetsel of Tennessee Eastman. Goddu explored a number of different applications including the measurement of epoxide functionality and unsaturation in polymers and phenolics. His review chapter published in 1960 included many of these applications. Whetsel also studied a number of applications including phenols, fuels, and polymers, and included those in a review article published in 1968.

Following these and other industrial applications of NIR in the 1950s–1960s, the field became somewhat stagnant for laboratory analyses with the advent of NMR and other newer technologies.
that had greater distinguishing capabilities. Online process instruments, especially for water or moisture measurements, were an exception. These came into use in the 1940s and continued through today, but they were primarily filter instruments measuring only a few specific wavelengths.

With the rise of NIR reflection instrumentation and chemometric data treatments for rapid, direct control measurements, the interest in NIR for industrial applications became greater again. Process control applications, either rapid laboratory measurements or real-time online analyses, benefited the most from the new technologies. Older applications, such as hydroxyl number, polymer properties, water measurement, and fuel analyses have been revisited.

13.2 HISTORY OF NIR FOR FOOD AND AGRICULTURE

It is generally recognized that the history of the application of NIR to the food and agricultural industry began with Karl Norris at the USDA. In fact, Karl Norris’ work was instrumental in the major renaissance of the NIR spectral region, especially with regard to its application to direct, solids-sampling measurements.

As Karl related in a recent review article,18 the first work was done beginning in 1949 using visible- to low-wavelength NIR radiation to grade eggs. An unpublished spectrum taken in 1952 showed a water overtone at about 750 nm, but the peak was not found to be useful in predicting egg quality, and he did not pursue NIR for about 10 years in favor of visible spectrometry for color sorting.

In 1962, Norris, Hart, and Golumbic first published an NIR application, the determination of moisture in methanol extracts of seeds.19 This was followed by transmission measurements of moisture in intact seeds with carbon tetrachloride used for reducing scattering losses.20 It was the leap to diffuse reflection, however, that propelled NIR spectroscopy to wide application in agriculture and, eventually, many other industries as well. This shift required instrument modifications and the segment/gap derivative multiple linear regression approach to calibration that was pioneered in Norris’s laboratory.

During the first stage in the development of NIR for food and agriculture, moisture analysis and nutrient determinations were driving forces. These measurements were important because the economic value of the products such as wheat is based on the dry weight and the protein content. Wet chemical methods for these analyses were costly and time-consuming, and not available at the points of sale. Early examples include the measurement of moisture in grain21 and soybeans.22

In Canada, Phil Williams23 of the Canadian Grain Commission purchased one of the first commercial instruments available and proceeded to initiate programs throughout his country to improve the measurement of moisture and protein in wheat. Similar efforts were launched in other large grain-producing countries such as Australia and Russia.

Applications in other agricultural products such as corn24 and tobacco25 followed. Forage analysis was another big driver of networked analyzer systems.26 The technology then rapidly spread to processed foods such as chocolate, baked goods, meat and dairy products, and snack foods. In Japan, the bulk of the NIR applications are in food and agriculture.27

Agricultural products were primarily dependent upon a small number of “protein,” fat, moisture, and carbohydrate wavelengths that were determined empirically through wavelength selection of large sample sets. In addition, the food and agricultural industries developed some nonchemical measurements, such as hardness of wheat, which was dependent upon particle size.28 There were some limited efforts to perform spectral band assignments, but most of the calibrations were empirical. The complexity of natural products discourages very specific band assignments. For example, the measurement of “protein” involves grouping many types of protein molecules. Early wavelengths used to measure protein, oil, and water were the combination bands at 2180 nm for protein, 2305 nm for oil, and 1940 nm for water.29 Tabulations of some general band assignments for foods and agricultural products can be found in the Osborne/Fearn and Williams/Norris books.
13.3 HISTORY OF NIR FOR PHARMACEUTICALS

NIR spectroscopy was used by pharmaceutical research groups at least since the late 1960s, initially to study hydrogen bonding of amines and amides or to perform quantitative analyses of these functional groups in solution. Examples include studies by S. Edward Krikorian at the University of Maryland, Yumiko Tanaka and Katsunosuke Machida of Kyoto University, and L. A. Strait and M. K. Hrenoff of the University of California, all from pharmacy departments. In 1966, Sinsheimer and Keuhnelian analyzed pharmaceutically active amine salts in pressed pellets. In 1967, Oi and Inaba determined phenacetin in preparations by NIR. In a 1977 article, Zappala and Post reported using solution NIR to measure meprobamate in tablets, capsules, suspensions, and injectables. This was an advantage over previous mid-infrared methodology because, in the NIR, the amine combination band at 1958 nm is separated from interference by hydroxyls and thus did not need to be chromatographically separated from an alcohol stabilizer.

The use of “modern” NIR in the pharmaceutical industry began soon after its use in the food and agricultural industries. Early applications included the measurement of moisture, particle size, the determination of composition, and identification of raw materials.

NIR moisture analyzers existed in industry long before the “modern” mode of multivariate NIR analysis, and the earliest applications of NIR in the pharmaceutical industry also began with moisture determinations. As examples, Beyer and Steffens measured water in excipients directly, and Sinsheimer and Poswalk looked at water by extracting into acetonitrile. Particle size was also a subject of early experiments. Although NIR spectroscopy alone cannot provide a particle size distribution the way other technologies such as image analysis, screening, and light scattering do, it is possible to estimate an average particle size by manipulating the underlying scattering curve. When coupled with low-angle light scattering, NIR has been shown to be quite accurate.

Quantitative analysis of tablets and other dosage forms were also performed early in the current wave of NIR. In 1982, Rose et al. reported the direct analysis of meglumine and meglumine diatrizoate in injectable solutions, for example. In 1986, Whitfield developed a method to measure the amount of lincomycin in granulations for veterinary purposes. This was the first NIR method accepted by the FDA as a primary method.

Whitfield’s article also represents an example of the use of discriminant analysis in pharmaceutical methods. Probably the first work in this field was done by Rose in 1982, when he showed that a number of structurally similar drugs could be identified. This was followed by the application of Mahalanobis distances to pharmaceutical raw materials.

A review of the uses of NIR in pharmaceuticals was done in 1987, and a chapter written in 1992 and revised in 2001. The field continues to expand.

REFERENCES


Appendix 1: NIR Absorption Band Charts — An Overview
FIGURE A1.1

Near Infrared C-H Stretch Vibrations - Harmonics

ALKANES
- Methyl Asymmetric
- Symmetric
- Methylene Asymmetric
- Symmetric

ALKENES
- Monosubstituted
- cis, disubstituted
- Trans, disubstituted
- Gem, disubstituted
- Trisubstituted

ALKYNES

AROMATICS

Nanometers

600 800 1000 1200 1400 1600 1800

5\nu 4\nu 3\nu 2\nu
FIGURE A1.2

Appendix 2a: Spectra–Structure Correlations—Labeled Spectra from 10,500 cm$^{-1}$ to 6300 cm$^{-1}$ (952 nm to 1587 nm)
<table>
<thead>
<tr>
<th>Compound Type Comparison</th>
<th>Second Combination Region CH</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Benzene, methyl, 99%</strong></td>
<td>3νC-H</td>
</tr>
<tr>
<td><strong>Pentane, 2,2,4-trimethyl, 99%</strong></td>
<td>CH₃, CH₃, 2ν₂CH₃ + δCH₃, 2ν₁CH₃ + δCH₃</td>
</tr>
<tr>
<td><strong>Undecane, 99%</strong></td>
<td>CH₃, CH₂, 2ν₂CH₂ + δCH₂, 2ν₁CH₂ + δCH₂</td>
</tr>
<tr>
<td><strong>3-Hexanone, 96%</strong></td>
<td>CH₃, CH₂, 2ν₂CH₂ + δCH₂, 2ν₁CH₂ + δCH₂</td>
</tr>
<tr>
<td><strong>2-Propanol, 2-methyl, 99.5%</strong></td>
<td>CH₃, 3νO-H (non-bonded)</td>
</tr>
<tr>
<td><strong>1-Decanamine, 97%</strong></td>
<td>CH₃, 3νN-H, CH₂, 2νN-H</td>
</tr>
</tbody>
</table>


FIGURE A2a.1
FIGURE A2a.2

FIGURE A2a.3

Diols

Third Combination Region CH

Second Combination Region CH

CH₃ CH₂

Absorbance

0.5
0.5
0.5
0.5

1.0
1.0
1.0
1.0

2,5-Hexanediol, 98%
1,2-Ethanediol, 99%
1,2-Propanediol, 99%
2,3-Butanediol
2,4-Pentanediol

**FIGURE A2a.4**

Butanediol Series

<table>
<thead>
<tr>
<th>2,3-Butanediol</th>
<th>3νO-H</th>
<th>CH₃</th>
<th>CH₂</th>
<th>2νO-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-Butanediol, 98%</td>
<td>10500</td>
<td>953</td>
<td>1111</td>
<td>1429</td>
</tr>
<tr>
<td>1,3-Butanediol, 99%</td>
<td>10500</td>
<td>1053</td>
<td>1176</td>
<td>1250</td>
</tr>
<tr>
<td>1,4-Butanediol, 98%</td>
<td>1111</td>
<td>1176</td>
<td>1333</td>
<td>1538</td>
</tr>
</tbody>
</table>

**Practical Guide to Interpretive Near-Infrared Spectroscopy**

**FIGURE A2a.5**

Ethers - 1

---

**Third Combination Region CH**

- Benzene, methoxy, 99%
- Ethane, 1,1,2-trimethoxy-, 99%
- Ethane, 1,1-dimethoxy-, 96%
- Ethane, 1,2-diethoxy-, 95%
- Propane, 2,2-dimethoxy-, 97%

**Second Combination Region CH**

- 3vC-H

---

Absorbance

- 1.0
- 0.5
- 0.0

Wavenumber (cm⁻¹)

- 10500
- 10000
- 9500
- 9000
- 8500
- 8000
- 7500
- 7000
- 6500

Wavenumber (Nm)

- 953
- 1000
- 1053
- 1111
- 1176
- 1250
- 1333
- 1429
- 1538

FIGURE A2a.6

Ethers - 2

Third Combination Region CH

Second Combination Region CH

3νC-H

Absorbance

Ethanol, 2-ethoxy-, 99%
Ethanol, 2-phenoxy-, 99%
Acetic acid, ethoxy-, 98%
Ethene, ethoxy-, 99%
Ethyne, ethoxy-

Practical Guide to Interpretive Near-Infrared Spectroscopy

FIGURE A2a.7

Pentanol Series

Second Combination Region CH

Third Combination Region CH

3νC-H

2νO-H

νC-H

10500 10000 9500 9000 8500 8000 7500 7000 6500 cm⁻¹

Absorbance

1.0

0.5

Cyclo pentanol, 99%

1-Pentanol, 99%

2-Butene-1,4-diol, 98.5%

2-Pentanol, 98%

2-Propen-1-ol, 98%

Cm⁻¹

Nm 953 1000 1053 1111 1176 1250 1333 1429 1538


FIGURE A2a.7
Spectra–Structure Correlations—Labeled Spectra

**FIGURE A2a.8**

Aldehydes

Third Combination Region CH

Second Combination Region CH

Pentanal, 98%
2-Propynal
Butanal, 99%
Decanal, 97%
Heptanal, 97%

FIGURE A2a.9

Ketone Examples

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexanone, 99%</td>
<td></td>
</tr>
<tr>
<td>2-Cyclohexen-1-one, 96%</td>
<td></td>
</tr>
<tr>
<td>2-Hexanone, 98%</td>
<td></td>
</tr>
<tr>
<td>2-Propanone, 99%</td>
<td></td>
</tr>
<tr>
<td>3-Hexanone, 96%</td>
<td></td>
</tr>
</tbody>
</table>

**FIGURE A2a.10**

*Butyl (C₄) Group Series - 1*

- Second Combination Region CH
- $2\nu_{\text{O-H}}$
- $2\nu_{\text{H-C}}$
- $\equiv C$
- $3\nu_{\text{C-H}}$

Excipients:
- Ethyle, ethanol: 99%
- 2-Butanol, 99%
- 2-Butanone, 99%
- Ethanol, 2-ethoxy, 99%
- Butanoic acid, 99%
- Ethene, ethoxy: 99%

Absorbance:

- Wavenumber (cm$^{-1}$): 4000 to 400
- Intensity (Mm): 0.5 to 1.0

Polyfunctional Series

3νC-H

Region CH

Second Combination

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzenepropanal, 98%</td>
<td>Ar-CH</td>
</tr>
<tr>
<td>2-Butenal, (E), 99%</td>
<td>3νH-C=C</td>
</tr>
<tr>
<td>2-Furanmethanol, 98%</td>
<td>3νH-C=C</td>
</tr>
<tr>
<td>2-Buten, 3-methyl-, 96%</td>
<td>3νH-C=C</td>
</tr>
<tr>
<td>2-Propenal, 3-phenyl-, (E)-, 98%</td>
<td>Ar-CH</td>
</tr>
</tbody>
</table>

Wavenumbers (cm⁻¹): 10500, 10000, 9500, 9000, 8500, 8000, 7500, 7000, 6500

3νH-O-H: 953, 1000, 1053, 1111, 1176, 1250, 1333, 1429, 1538


FIGURE A2a.11
**FIGURE A2a.12**

**Substituted Aromatic Aldehydes**

- Benzaldehyde, 99%
- Benzaldehyde, 2,4,6-trimethyl-, 98%
- Benzaldehyde, 2,4-dimethyl-, 98%
- Benzaldehyde, 2-bromo-, 98%
- Benzaldehyde, 2-chloro-, 98%


**Second Combination Region CH**

- $3\nu C-H$

Absorbance

<table>
<thead>
<tr>
<th>Cm$^{-1}$</th>
<th>10500</th>
<th>10000</th>
<th>9500</th>
<th>9000</th>
<th>8500</th>
<th>8000</th>
<th>7500</th>
<th>7000</th>
<th>6500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nm</td>
<td>953</td>
<td>1053</td>
<td>1111</td>
<td>1176</td>
<td>1250</td>
<td>1333</td>
<td>1429</td>
<td>1538</td>
<td></td>
</tr>
</tbody>
</table>
FIGURE A2a.13

Alkanes

Third Combination Region CH

Second Combination Region CH

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dodecane</td>
<td>99%</td>
</tr>
<tr>
<td>Hexane</td>
<td>97%</td>
</tr>
<tr>
<td>Octadecane</td>
<td>98%</td>
</tr>
<tr>
<td>Octane</td>
<td>99%</td>
</tr>
<tr>
<td>Pentane</td>
<td>99%</td>
</tr>
</tbody>
</table>

Absorbance


FIGURE A2a.13
Butyl (C4) Group Series

Second Combination Region CH

2ν O-H

3ν C-H

Butane, 2-iodo-, 99%
1-Butanol, 99%
Butane, 1-chloro-, 99%
Butane, 2-bromo-, 99%
2-Butanol, 99%
Butane, 2-chloro-, 99%

Absorbance

1.0
0.5
1.0
0.5
1.0
0.5
1.0
0.5
1.0
0.5
1.0
0.5

FIGURE A2a.16

Ethyl (C2) Group Series

Second Combination Region CH

Ethane, nitro-, 97%
Ethane, 1,1,1-trichloro-, 94%
Ethane, 1,2-dibromo-, 99%
Ethane, 1,2-dichloro-, 99%
Ethanol, 2-bromo-, 97%

Absorbance

\[ \text{Cm}^{-1} \quad 10500 \quad 10000 \quad 9500 \quad 9000 \quad 8500 \quad 8000 \quad 7500 \quad 7000 \quad 6500 \]

\[ \text{Nm} \quad 953 \quad 1000 \quad 1053 \quad 1111 \quad 1176 \quad 1250 \quad 1333 \quad 1429 \quad 1538 \]


FIGURE A2a.16
FIGURE A2a.17

Isomerism Series

Second Combination Region CH

3vC-H

Pentane, 99%

Pentane, 2,2,4-trimethyl, 99%

Pentane, 2-methyl, 98%

Heptane, 99%

Absorbance

Cm⁻¹

Nm

953

10500

10000

9500

9000

8500

8000

7500

7000

6500

1053

1111

1176

1250

1333

1429

1538

FIGURE A2a.18

Methyl Group Series

Second Combination Region CH

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorbance</th>
<th>Wave Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane, nitro-, 98%</td>
<td>3vC-H</td>
<td>284</td>
</tr>
<tr>
<td>Silane, dichloromethyl-, 99%</td>
<td>3vSi-H</td>
<td>392</td>
</tr>
<tr>
<td>Formic acid, methyl ester, 97%</td>
<td>3vH-C=O</td>
<td>454</td>
</tr>
<tr>
<td>Methanol, 99%</td>
<td>2vO-H</td>
<td>1701</td>
</tr>
</tbody>
</table>

FIGURE A2a.19

Propyl (C₃) Group Series

Second Combination Region CH₂

3νC-H

CH₃

2νO-H

2νO-H

CH₃

2-Propanol, 99%

Propane, 1-chloro-, 98%

1-Propanol, 99%

Propane, 2-chloro-, 99%

Cycloalkenes

Second Combination Region CH

3νC-H

<table>
<thead>
<tr>
<th>1.0</th>
<th>Cyclopentene, 99%</th>
<th>3νH-C=C</th>
<th>CH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>Cycloheptene, 93%</td>
<td>3νH-C=C</td>
<td>CH₃</td>
</tr>
<tr>
<td>0.5</td>
<td>Cyclohexene, 99%</td>
<td>3νH-C=C</td>
<td>CH₂</td>
</tr>
<tr>
<td>0.5</td>
<td>Cyclooctene, (Z)-, 95%</td>
<td>3νH-C=C</td>
<td>CH₂</td>
</tr>
</tbody>
</table>


FIGURE A2a.20
Alkene Series

Second Combination
Region CH

$\nu_{C=\overset{*}{C}}$

$3\nu_{C-H}$

1-Decene, 96%
1-Hexene, 96%
1-Octene, 97%
1-Pentene, 98%
1-Tetradecene, 95%

Absorbance

$Cm^{-1}$

<table>
<thead>
<tr>
<th>Nm</th>
<th>953</th>
<th>1000</th>
<th>1053</th>
<th>1111</th>
<th>1176</th>
<th>1250</th>
<th>1333</th>
<th>1429</th>
<th>1538</th>
</tr>
</thead>
<tbody>
<tr>
<td>10500</td>
<td>1111</td>
<td>1176</td>
<td>1250</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10000</td>
<td>1111</td>
<td>1176</td>
<td>1250</td>
<td>1333</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9500</td>
<td>1111</td>
<td>1176</td>
<td>1250</td>
<td>1333</td>
<td>1429</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9000</td>
<td>1111</td>
<td>1176</td>
<td>1250</td>
<td>1333</td>
<td>1429</td>
<td>1538</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


FIGURE A2a.21
Internal vs. Terminal Alkenes

Second Combination Region CH

3vC-H

1-Butene, 3,3-dimethyl-, 98%

2-Butene, 2,3-dimethyl-, 97%

2-Butene, 2-methyl-, 93%

Absorbance

Cm⁻¹ 10500 10000 9500 9000 8500 8000 7500 7000 6500
Nm   953 1053 1176 1250 1333 1429 1538


FIGURE A2a.22
FIGURE A2a.23

Alkynes

Second Combination Region CH

3νC-H

CH₃, CH₂

4-Octyne, 99%
1-Octyne, 98%
1-Pentyne, 98%
2-Butyne, 99%
1-Propyne, 3-chloro-, 97%

FIGURE A2a.24

Comparative X-H Series

Second Combination
Region CH

3vC-H

FIGURE A2a.25

Alkyl Amines

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Propanamine, N, N-dipropyl, 98%</td>
<td>1.0</td>
</tr>
<tr>
<td>1,2-Propanediamine, 98%</td>
<td>1.0</td>
</tr>
<tr>
<td>1,7-Heptanedianiline, 98%</td>
<td>1.0</td>
</tr>
<tr>
<td>1-Decanamine, 97%</td>
<td>1.0</td>
</tr>
<tr>
<td>Cyclododecanamine, 98%</td>
<td>1.0</td>
</tr>
<tr>
<td>1,4-Butanedianiline, N, N', N'-tetramethyl-, 98%</td>
<td>1.0</td>
</tr>
</tbody>
</table>

FIGURE A2a.26

Aryl Amines

Second Combination Region CH

3νC-H

FIGURE A2a.27

Amides -1

Second Combination Region CH

3vC-H

3vN-H doublet

Absorbance

Acetamide, N-methyl-, 98%

3vN-H

CH$_3$

2vN-H

Formamide, 98%

3vN-H

CH$_3$

2vN-H

Phosphoric triamide, hexamethyl-, 98%

CH$_3$

2-Propenamide, N, N-dimethyl-, 98%

3vN-H

3vH-C=C

CH$_3$

CH$_2$


FIGURE A2a.27
FIGURE A2a.28

**Amino Acids and Proteins**

### Second Combination Region CH

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorbance</th>
<th>Cm⁻¹</th>
<th>Nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycine, N-formyl-, ethyl ester, 98%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D-Valine, 3-methyl-, 1,1-dimethylethyl ester, 99%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L-Valine, 3-methyl-, 1,1-dimethylethyl ester, 99%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**FIGURE A2a.29**

Aromatic with N and S

Second Combination Region CH

3\nuC-H

Absorbance

Thiophene, 99%
1H-Pyrrole, 1-methyl, 99%
Pyridine, 4-methyl, 97%
1H-Indole, 99%
Quinoline, 97%

10500 10000 9500 9000 8500 8000 7500 7000 6500

953 1000 1053 1111 1176 1250 1333 1429 1538


FIGURE A2a.30
FIGURE A2a.31

Aliphatic Series

3vC-H

Region CH

Absorbance

Octane, 99%
1,7-Octadiene, 98%
Pentane, 2,2,4-trimethyl-, 99%
Cyclohexane, 99.5%
Cyclohexene, 99%

Cm⁻¹  10500  10000  9500  9000  8500  8000  7500  7000  6500
Nm    953    1000   1053   1111   1176   1250   1333   1429   1538

Aromatics - 1

Second Combination Region CH

3vC-H

Benzaldehyde, 99%

Benzene, 99.7%

Benzene, methyl-, 99%

Absorbance

Cm\(^{-1}\)  10500  10000  9500  9000  8500  8000  7500  7000  6500
Nm   953  1000  1053  1111  1176  1250  1333  1429  1538

3vH-C=O

Ar-CH

Ar-CH

CH\(_3\)


FIGURE A2a.32
Aromatics - 2

3νC-H

Region CH

2νO-H

Phenol, 3-methyl, 99%

1,1'-Biphenyl, 99%

Benzene, 1,2-dimethyl-

Benzene, 1,4-dimethyl, 99%

Phenol, 2,4,5-trichloro-, 99%

Phenol, 2-ethyl-, 98%

Absorbance

ν

C-H


FIGURE A2a.33
FIGURE A2a.34


Aromatics - 3

Phenanthrene 99%
Phenol, 4-methyl-, 98%
Benzene, bromo-, 99%
Benzene, methyl-, 99%
Naphthalene, 99%
Benzene, nitro-, 99%

Second Combination
Region CH

Absorbance

Cm<sup>-1</sup> 10500 10000 9500 9000 8500 8000 7500 7000 6500
Nm 953 1000 1053 1111 1176 1250 1333 1429 1538
Cyclic Ethers

3νC-H

Second Combination Region CH

4H-Pyran-4-one, tetrahydro-, 98%
2H-Pyran, 3,4-dihydro-, 98%
Furan, 99%
2H-Pyran, tetrahydro-, 99%

Absorbance

νC-H

953 1000 1053 1111 1176 1250 1333 1538

Cm⁻¹


FIGURE A2a.35
Comparison Series

Acetamide, N-methyl-, 98%

1-Propen-2-ol, acetate, 99%

Ethanol, 2-ethoxy-, acetate, 99%

Acetic acid, 99%

Second Combination Region CH

Absorbance

Cm⁻¹

Nm

953
1000
1053
1111
1176
1250
1333
1429
1538

2vN-H

3vN-H

3vC-H

2vO-H

3vH-C=C


FIGURE A2a.36
Figure A2a.37: Carboxylic Acids

- **Propanoic acid, 99%**: peaks at 2νO-H, 3νH-C=O, CH3, CH2
- **Dodecanoic acid, 99%**: peaks at 2νO-H, 3νH-C=O, CH3, CH2
- **Formic acid, 98%**: peaks at 2νO-H, 3νH-C=O
- **Benzoic acid, methyl ester, 98%**: peaks at Ar-CH, CH3

Absorbance

<table>
<thead>
<tr>
<th>( \text{Cm}^{-1} )</th>
<th>10500</th>
<th>10000</th>
<th>9500</th>
<th>9000</th>
<th>8500</th>
<th>8000</th>
<th>7500</th>
<th>7000</th>
<th>6500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nm</td>
<td>953</td>
<td>1000</td>
<td>1053</td>
<td>1111</td>
<td>1176</td>
<td>1250</td>
<td>1333</td>
<td>1429</td>
<td>1538</td>
</tr>
</tbody>
</table>


**FIGURE A2a.37**
Spectra–Structure Correlations—Labeled Spectra

FIGURE A2a.38

Heterocyclic Compounds

Absorbance

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percentage</th>
<th>Cm⁻¹</th>
<th>Nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiophene, 99%</td>
<td>10500</td>
<td>953</td>
<td></td>
</tr>
<tr>
<td>1H-Indole, 99%</td>
<td>10000</td>
<td>1053</td>
<td></td>
</tr>
<tr>
<td>1H-Pyrrole, 1-methyl, 99%</td>
<td>9500</td>
<td>1111</td>
<td></td>
</tr>
<tr>
<td>Pyridine, 2-bromo-, 98%</td>
<td>9000</td>
<td>1176</td>
<td></td>
</tr>
<tr>
<td>Pyridine, 3-ethyl-, 98%</td>
<td>8500</td>
<td>1250</td>
<td></td>
</tr>
<tr>
<td>Furan, 99%</td>
<td>8000</td>
<td>1333</td>
<td></td>
</tr>
<tr>
<td>Quinoline, 97%</td>
<td>7500</td>
<td>1429</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7000</td>
<td>1538</td>
<td></td>
</tr>
</tbody>
</table>

FIGURE A2a.39

Five-Membered Ring Heterocyclic Compounds

- Thiazole, 4,5-dihydro-2-(methylthio)-, 98%
- Thiazolidine, 2,2-dimethyl-, 98%
- Thiazole, 4,5-dihydro-2-(2-propenythio)-, 99%

**FIGURE A2a.40**

**Functional Group Comparisons**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undecane, 99%</td>
<td></td>
</tr>
<tr>
<td>1-Decanamine, 97%</td>
<td></td>
</tr>
<tr>
<td>Pentane, 2,2,4-trimethyl-, 99%</td>
<td></td>
</tr>
<tr>
<td>2-Propanol, 2-methyl-, 99.5%</td>
<td></td>
</tr>
<tr>
<td>3-Hexanone, 96%</td>
<td></td>
</tr>
<tr>
<td>Benzene, 99.7%</td>
<td></td>
</tr>
<tr>
<td>Benzene, methyl-, 99%</td>
<td></td>
</tr>
</tbody>
</table>

**Second Combination Region CH**

- $3\nu$C-H
- $2\nu$N-H
- $3\nu$O-H
- $2\nu$O-H
- $4\nu$C=O


**FIGURE A2a.40**
Polyenes

FIGURE A2a.41


158
FIGURE A2a.42

Polymers and Rubbers -1

2νCH

First Combination Region CH

3νCH

Second Combination Region CH

Absorbance

Cm⁻¹

Nm

9000 8000 7000 6000 5000 4000

1111 1250 1429 1667 2000 2500

Ethylene Vinyl Acetate

60% Polypropylene/40% Polyester

60% Polypropylene-Polyethylene copolymer and 40% Polyester

Atactic Polypropylene


FIGURE A2a.42
Polymers and Rubbers - 2

First Combination Region CH

Polyacrylic acid

Second Combination Region CH

Styrene isoprene styrene

2νCH

Polymer

Polyacrylic acid

Styrene, Ethylene, Styrene Copolymer

Starch

Interference fringes

Silicone

Styrene isoprene styrene

νO-H + δO-H

νO-H + δO-H

νO-H + δO-H

Cm⁻¹ 9000 8000 7000 6000 5000 4000
Nm  1111  1250  1429  1667  2000  2500


FIGURE A2a.43
FIGURE A2a.44

Polymer Pellets - 1

3.0

2.5

3.0

Cellulose acetate

Cellulose acetate butyrate

Ethyl cellulose

Polyethylene, chlorinated (25% Cl)

Poly(ethylene oxide)

Poly(isobutyl methacrylate)

Polypropylene, isotactic, chlorinated

Cellulose acetate

Cellulose acetate butyrate

Ethyl cellulose

Polyethylene, chlorinated (25% Cl)

Poly(ethylene oxide)

Poly(isobutyl methacrylate)

Absorbance

cm⁻¹

nm

4000

3000

2500

3000

2500

2000

1500

1000

500

200

150

10

## FIGURE A2a.45

**Polymer Pellets - 2**

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>FOURTH Combination Region CH</th>
<th>THIRD Combination Region CH</th>
<th>SECOND Combination Region CH</th>
<th>FIRST Combination Region CH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(vinylidene fluoride)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Absorbance</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Cellulose propionate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Absorbance</td>
<td>3.0</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Poly(vinyl butyral)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Absorbance</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Absorbance</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Poly(vinyl pyrrolidone)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Absorbance</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Poly(vinyl stearate)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Absorbance</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>


### Absorbance Values
- Poly(vinylidene fluoride): 2.5
- Cellulose propionate: 3.0
- Poly(vinyl butyral): 2.5
- Poly(vinyl chloride): 2.5
- Poly(vinyl pyrrolidone): 2.5
- Poly(vinyl stearate): 2.5

### Wavenumber (Nm)
- 625
- 715
- 833
- 1000
- 1250
- 1667
- 2500

### Wavenumber (Cm⁻¹)
- 15000
- 14000
- 12000
- 10000
- 8000
- 6000
- 4000
Appendix 2b: Spectra–Structure Correlations—Labeled Spectra from 7200 cm$^{-1}$ to 3800 cm$^{-1}$ (1389 nm to 2632 nm)
Compound Type Comparison

<table>
<thead>
<tr>
<th>Compound Type Comparison</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2νC-H</td>
</tr>
</tbody>
</table>

**First Combination Region CH**

- Benzene, methyl-, 99%
  - Ar-CH
- Pentane, 2,2,4-trimethyl-, 99%
  - CH₃
- Undecane, 99%
  - CH₃
- 3-Hexanone, 96%
  - 4νC=O
- 2-Propanol, 2-methyl-, 99.5%
  - 2νO-H
- 1-Decanamine, 97%
  - 2νN-H


FIGURE A2b.1
FIGURE A2b.2

Alcohols

First Combination Region CH

2νC-H

Absorbance

Methanol, 99%

1-Butanol, 99%

2-Propanol, 2-methyl-, 99.5%

2-Propanol, 99%

3-Pentanol, 98%

Cm⁻¹

Nm

7000 6500 6000 5500 5000 4500 4000

1538 1667 1818

2000 2222 2500


FIGURE A2b.2
FIGURE A2b.3

Diols

First Combination Region CH

2νC-H

2.5-Hexanediol, 98%
1,2-Ethanediole, 99%
1,2-Propanediol, 99%
2,3-Butanediol
2,4-Pentanediol

Absorbance

Cm⁻¹

7000 6500 6000 5500 5000 4500 4000

Nm

1429 1538 1667 1818 2000 2222 2500


FIGURE A2b.3
Butanediol Series

First Combination Region CH

2νC-H

Absorbance

1.0

0.5

0.5

1.0

Cm⁻¹

Nm

7000

6500

6000

5500

5000

4500

4000

2000

2222

2500

2,3-Butanediol

1,2-Butanediol, 98%

1,3-Butanediol, 99%

1,4-Butanediol, 98%

νOH + δOH


FIGURE A2b.4
FIGURE A2b.5

Ethers - 1

Absorbance

1.0
0.5

Benzene, methoxy-, 99%
Ethane, 1,1,2-trimethoxy-, 99%
Ethane, 1,1-dimethoxy-, 96%
Ethane, 1,2-diethoxy-, 95%
Propane, 2,2-dimethoxy-, 97%

2νC-H

First Combination Region CH

Cm⁻¹
Nm

7000 6500 6000 5500 5000 4500 4000
1429 1538 1667 1818 2000 2222 2500


FIGURE A2b.5
First Combination Region CH

Ethanol, 2-ethoxy-, 99%
Ethanol, 2-phenoxy-, 99%
Acetic acid ethoxy-, 98%
Ethene, ethoxy-, 99%
Ethyne, ethoxy-

Absorbance

$\nu_{\text{CH}}$, $2\nu_{\text{CH}}$, $\nu_{\text{OH}} + \delta_{\text{OH}}$


FIGURE A2b.6
FIGURE A2b.7

FIGURE A2b.8

Aldehydes

2νC-H

First Combination Region CH

Absorbance

Pentanal, 98%

2-Propynal

Butanal, 99%

Decanal, 97%

Hexanal, 98%

Cm⁻¹

7000 6500 6000 5500 5000 4500 4000

Nm

1429 1538 1667 1818 2000 2222 2500

δCH + 2νC=O

νC=O + νCH and 2δCH + νC=O

4νC=O

νC=O

3νC=O

2νH-C≡C

2νC-H

νC=O

CH2

CH3


FIGURE A2b.8
FIGURE A2b.9

FIGURE A2b.10

First Combination Region CH

2νC-H

Butyl (C4) Series -1

Ethyne, ethoxy-
2-Butanol, 99%
2-Butanone, 99%
Ethanol, 2-ethoxy-, 99%
Butanoic acid, 99%

Absorbance

νOH + δOH
νOH + δOH
νC=O
3νC-H
2νH-C

Cm⁻¹
6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500

FIGURE A2b.11

Polyfunctional Series

First Combination Region CH

FIGURE A2b.12

Substituted Aromatic Aldehydes

Benzaldehyde, 99%
Benzaldehyde, 2,4,6-trimethyl-, 98%
Benzaldehyde, 2,4-dimethyl-, 98%
Benzaldehyde, 2-bromo-, 98%
Benzaldehyde, 2-chloro-, 98%

2νC-H, δCH in-plane + νC-C, νAr-CH + δAr-CH

Absorbance

Cm⁻¹
Nm
7000 6500 6000 5500 5000 4500 4000
1429 1538 1667 1818 2000 2222 2500

νC=O, υAr-CH, δAr-CH, 2νC-H, νC-C

**FIGURE A2b.13**

Butyl (C4) Group Series - 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butane, 2-iodo-, 99%</td>
<td>0.5</td>
</tr>
<tr>
<td>1-Butanol, 99%</td>
<td>1.0</td>
</tr>
<tr>
<td>Butane, 1-chloro-, 99%</td>
<td>0.5</td>
</tr>
<tr>
<td>Butane, 2-bromo-, 98%</td>
<td>1.0</td>
</tr>
<tr>
<td>2-Butanol, 99%</td>
<td>0.5</td>
</tr>
<tr>
<td>Butane, 2-chloro-, 98%</td>
<td>1.0</td>
</tr>
</tbody>
</table>


FIGURE A2b.14
FIGURE A2b.15


FIGURE A2b.15
**Ethyl (C2) Group Series**

**First Combination Region CH**

- Ethane, nitro-\(, 97\%\)
- Ethane, 1,1,1-trichloro-\(, 94\%\)
- Ethane, 1,2-dibromo-\(, 99\%\)
- Ethane, 1,2-dichloro-\(, 99\%\)
- Ethanol, 2-bromo-\(, 97\%\)

**Absorbance**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane, nitro-(, 97%)</td>
<td>1.0</td>
</tr>
<tr>
<td>Ethane, 1,1,1-trichloro-(, 94%)</td>
<td>1.0</td>
</tr>
<tr>
<td>Ethane, 1,2-dibromo-(, 99%)</td>
<td>1.0</td>
</tr>
<tr>
<td>Ethane, 1,2-dichloro-(, 99%)</td>
<td>1.0</td>
</tr>
<tr>
<td>Ethanol, 2-bromo-(, 97%)</td>
<td>1.0</td>
</tr>
</tbody>
</table>


**FIGURE A2b.16**
Isomerism Series

2νCH

First Combination Region CH

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane, 99%</td>
<td>1.0</td>
</tr>
<tr>
<td>Pentane, 2,2,4-trimethyl, 99%</td>
<td>0.5</td>
</tr>
<tr>
<td>Pentane, 2-methyl, 98%</td>
<td>1.0</td>
</tr>
<tr>
<td>Heptane, 99%</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Cm⁻¹  | 7000  | 6500  | 6000  | 5500  | 5000  | 4500  | 4000  |
Nm    | 1429  | 1538  | 1667  | 1818  | 2000  | 2222  | 2500  |


FIGURE A2b.17
Methyl (C) Group Series

First Combination Region CH

Absorbance

7000 6500 6000 5500 5000 4500 4000

Cm⁻¹

1429 1538 1667 1818 2000 2222 2500


FIGURE A2b.18
Propyl (C3) Group Series

2νC-H

First Combination Region CH

Absorbance

Cm⁻¹

7000
6500
6000
5500
5000
4500
4000

Nm

1429
1538
1667
1818
2000
2222
2500

2-Propanol, 99%
Propane, 1-chloro-, 98%
1-Propanol, 99%
Propane, 2-chloro-, 99%

νOH + δOH

νOH + δOH

2νO-H


FIGURE A2b.19
FIGURE A2.20

Cm⁻¹

Absorbance

2\(\delta_s\)\(\text{H-C}\)

2\(\nu_s\)\(\text{H-C}\)

2\(\nu_a\)\(\text{H-C}\)

2\(\delta_a\)\(\text{H-C}\)

Alkenes

1.0 1-Decene, 96%
1.0 1-Hexene, 96%
1.0 1-Octene, 97%
1.0 1-Pentene, 98%
1.0 1-Tetradecene, 95%

**Cycloalkenes**

![Spectra](image)

- **2νC-H**
- **2δ_αHC=C**

**Figure A2b.21**

**Cyclopentene, 99%**

**Cycloheptene, 93%**

**Cyclohexene, 99%**

**Cyclooctene, (Z)-, 95%**

Absorbance

<table>
<thead>
<tr>
<th>Cm⁻¹</th>
<th>7000</th>
<th>6500</th>
<th>6000</th>
<th>5500</th>
<th>5000</th>
<th>4500</th>
<th>4000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nm</td>
<td>1429</td>
<td>1538</td>
<td>1667</td>
<td>1818</td>
<td>2000</td>
<td>2222</td>
<td>2500</td>
</tr>
</tbody>
</table>

1-Butene, 3,3-dimethyl-, 98%
2-Butene, 2,3-dimethyl-, 97%
2-Butene, 2-methyl-, 93%

Internal vs. Terminal Alkenes

First Combination Region CH

Absorbance


FIGURE A2b.22
FIGURE A2b.23


FIGURE A2b.23
FIGURE A2b.24

Comparative X-H Series

Absorbance vs. Wavenumber (cm⁻¹)

- Pentane, 99%
- 1-Butanamine, 99%
- 2-Butanethiol, 95%
- 2-Butanol, 99%
- 2-Propanamine, 99%

First Combination Region CH
- νC-H
- 2νC-H
- νN-H + δN-H
- 2νN-H
- νO-H + δO-H
- 3δN-H
- νNH + δNH
- νOH + δOH
- νNH + δNH

**FIGURE A2b.25**

Alkyl Amines

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Propanamine, N,N-dipropyl, 98%</td>
<td>1.0</td>
</tr>
<tr>
<td>1,2-Propanediamine, 98%</td>
<td>1.0</td>
</tr>
<tr>
<td>1,7-Heptanediamine, 98%</td>
<td>1.0</td>
</tr>
<tr>
<td>1-Decanamine, 97%</td>
<td>1.0</td>
</tr>
<tr>
<td>Cyclododecanamine, 98%</td>
<td>1.0</td>
</tr>
<tr>
<td>1,4-Butanediame, N,N,N',N'-tetramethyl, 98%</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Aryl Amines

- 1,3-Benzenediamine, N, N-dimethyl, 98%
- 2-Pyridinemethanol, 98%
- Pyridine, 4-methyl, 97%
- Benzenamine, 99%
- 1H-Indole, 99%

Absorbance

- 2$\nu_2$N-H
- 2$\nu_2$C-H
- $\nu$NH + $\delta$NH
- 3$\delta$N-H

First Combination Region CH


FIGURE A2b.26
Amides - 1

First Combination Region CH

<table>
<thead>
<tr>
<th>Compound</th>
<th>2νC-H</th>
<th>νC=O + νCH</th>
<th>νNH + δNH</th>
<th>2νC=O + νCN</th>
<th>3δN-H</th>
<th>νC=O + νCH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetamide, N-methyl-, 98%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formamide, 98%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphoric triamide, hexamethyl-, 98%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Propenamide, N, N-dimethyl-, 98%</td>
<td>2νN-H</td>
<td></td>
<td></td>
<td>2νHC=C</td>
<td>28 HC=C</td>
<td></td>
</tr>
</tbody>
</table>

Cm⁻¹ 7000 6500 6000 5500 5000 4500 4000
Nm  1429 1538 1667 1818 2000 2222 2500


FIGURE A2b.27
FIGURE A2b.28

Spectra–Structure Correlations—Labeled Spectra

First Combination Region CH

2νC-H

Amides-2

1.0 Propanamide, N-methyl-, 98%
0.5 Benzamide, N,N-diethyl-3-methyl-, 98%
1.0 Butanamide, N,N-diethyl-3-oxo-, 99%
1.0 Acetamide, N-methyl-, 98%
1.0 Formamide, N-methyl-, 99%

0.5

Absorbance

Cm-1

FIGURE A2b.29


FIGURE A2b.29
FIGURE A2b.30

Heterocyclics with N and S

2ν_s C-H

First Combination Region CH

FIGURE A2b.31

Aliphatic Series

First Combination Region CH

2νC-H

FIGURE A2b.32

FIGURE A2b.33

Aromatics - 2

Absorbance

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percentage</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol, 3-methyl, 99%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,1'-Biphenyl, 99%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene, 1,3-dimethyl, 98%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene, 1,4-dimethyl, 99%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol, 2,4,5-trichloro, 99%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol, 2-ethyl, 98%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

First Combination Region CH

2νC-H


FIGURE A2b.33
Aromatic Examples - 3

2νC-H Region CH

- Phenanthrene, 99%
- Phenol, 4-methyl-, 98%
- Benzene, bromo-, 99%
- Benzene, methyl-, 99%
- Naphthalene, 99%
- Benzene, nitro-, 99%

Absorbance

Cm⁻¹: 7000, 6500, 6000, 5500, 5000, 4500, 4000
Nm: 1429, 1538, 1667, 1818, 2000, 2222, 2500

FIGURE A2b.35

Carbon-Oxygen Heterocyclics


FIGURE A2b.35
<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetamide, N-methyl, 98%</td>
<td>1.0</td>
</tr>
<tr>
<td>1-Propen-2-ol, acetate, 99%</td>
<td>0.5</td>
</tr>
<tr>
<td>Ethanol, 2-ethoxy, acetate, 99%</td>
<td>0.5</td>
</tr>
<tr>
<td>Acetic acid, 99%</td>
<td>0.5</td>
</tr>
</tbody>
</table>


**FIGURE A2b.36**
**Carboxylic Acid Series**

- **Propanoic acid, 99%**
- **Dodecanoic acid, 99%**
- **Formic acid, 98%**
- **Benzoic acid, methyl ester, 98%**

![Spectra](image)

First Combination Region CH

Absorbance

- **OH**
- **Sloping baseline**
- **C-H**


**FIGURE A2b.37**
FIGURE A2b.38

Heterocyclic Compounds

2νC-H

First Combination Region CH

Absorbance

Thiophene, 99%
1H-Indole, 99%
2v, N-H
1H-Pyrrole, 1-methyl, 99%
Pyridine, 2-bromo-, 98%
Pyridine, 3-ethyl-, 98%
Furan, 99%
Quinoline, 97%

Cm⁻¹

7000 6500 6000 5500 5000 4500 4000

Nm

1429 1538 1667 1818 2000 2222 2500


FIGURE A2b.38
204

Practical Guide to Interpretive Near-Infrared Spectroscopy

FIGURE A2b.39

Five-Membered Ring Heterocyclic Compounds

2νC-H

First Combination Region CH

Absorbance

Thiazole, 4,5-dihydro-2-(methylthio), 98%

Thiazolidine, 2,2-dimethyl-, 98%

Thiazole, 4,5-dihydro-2-(2-propenylthio), 99%

νC-H

2νN-H

FIGURE A2b.40

Hydrocarbon Comparisons

Absorbance

2νC-H

First Combination Region CH

1.0

Undecane, 99%

1-Decanamine, 97%

Pentane, 2,2,4-trimethyl-, 99%

2-Propanol, 2-methyl-, 99.5%

3-Hexanone, 96%

Benzene, 99.7%

Benzene, methyl-, 99%

νNH + δNH

3νN-H

2νN-H

νC-H

3νC=O

4νC=O

2νCH + νCCC

Cm⁻¹

Nm

7000 6500 6000 5500 5000 4500 4000

1429 1538 1667 1818 2000 2222 2500

FIGURE A2b.41

Polyenes

Absorbance

1,3-Butadiene, 2-methyl, 98%

1,3,5-Cycloheptatriene, 93%

1,3-Cyclohexadiene, 98%

1,3-Cyclooctadiene, 98%

1,5-Hexadiene, 97%

Appendix 3: Detailed Spectra–Structure Correlations—Overlapping Spectra from 10,500 cm\(^{-1}\) to 3800 cm\(^{-1}\) (952 nm to 2632 nm)
Alcohols

FIGURE A3.1


FIGURE A3.2

FIGURE A3.3

Absorbance spectra of alcohols showing the characteristic peaks for hydroxyl (2νO-H) and methylene (2νC-H) vibrations. Peaks A, B, and C correspond to specific functional groups in the alcohols:

- **HO$_2^-$** and HO$_2^+$
- CH$_3$
- CH$_2$

Various alcohols are shown, including 2,3-Butanediol, Methanol, 99%, 1-Butanol, 99%, and others. The spectra are used by permission from "NIR Spectra of Organic Compounds" © Wiley-VCH, ISBN 3-527-31630-2.
FIGURE A3.4

Alcohols - diols

Absorbance

2νO-H

2νC-H

Dioxane

1,2-Butanediol, 98% A
1,3-Butanediol, 99% B
1,4-Butanediol, 98% C
2,3-Butanediol D

First Combination Region CH


FIGURE A3.4
**FIGURE A3.5**


**Ethers**

- Ethane, 1,1,2-trimethoxy, 99%
- Propane, 2,2-dimethoxy, 97%
- Benzene, methoxy, 99%

**3νC-H**

- CH₃
- CH₂
- CH-O

**Third Combination Region CH**

**Second Combination Region CH**
FIGURE A3.6

Detailed Spectra–Structure Correlations—Overlapping Spectra


Ethers

Absorbance

Cm⁻¹

Nm

7000

6000

5000

4000

3000

2000

1000

7000

4000

1000

6000

3000

2000

1000

7000

4000

1000

6000

3000

2000

1000

7000

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2000

1000
Detailed Spectra–Structure Correlations—Overlapping Spectra

FIGURE A3.8


FIGURE A3.8
Aldehydes


FIGURE A3.9
Detailed Spectra–Structure Correlations—Overlapping Spectra

FIGURE A3.10

C-H types comparison


FIGURE A3.11
Detailed Spectra–Structure Correlations—Overlapping Spectra

FIGURE A3.12

C-H types comparison

Second Combination Region CH

Absorbance

Pentane, 2,2,4-trimethyl-, 99%  
Benzene, 99.7%
Cyclohexane, 99.5%  
Octane, 99%


FIGURE A3.12
C-H types comparison

FIGURE A3.13

**FIGURE A3.14**

C-H types comparison

2vC-H

Absorbance

First Combination Region CH

Benzene, 99.7%

Cyclohexane, 99.5%

Octane, 99%

Pentane, 2,2,4-trimethyl, 99%

<table>
<thead>
<tr>
<th>Cm⁻¹</th>
<th>Nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>7000</td>
<td>1429</td>
</tr>
<tr>
<td>6500</td>
<td>1538</td>
</tr>
<tr>
<td>6000</td>
<td>1667</td>
</tr>
<tr>
<td>5500</td>
<td>1818</td>
</tr>
<tr>
<td>5000</td>
<td>2000</td>
</tr>
<tr>
<td>4500</td>
<td>2222</td>
</tr>
<tr>
<td>4000</td>
<td>2500</td>
</tr>
</tbody>
</table>

Alkenes

$3\nu H-C=C^*$

Second Combination Region CH

Third Combination Region CH


FIGURE A3.15
Alkenes

FIGURE A3.16

Absorbance

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1

1-Nonene, 97%
1-Decene, 96%
1-Heptene, 96%

$\nu_{H-C=C}^*$

$2\nu_{C-H}$

$3\nu_{C=C}$

$\nu_{C=CH}$

First Combination Region CH

Cm$^{-1}$
Nm

7000 1429
6500 1538
6000 1667
5500 1818
5000 2000
4500 2222
4000 2500


FIGURE A3.16
FIGURE A3.17

Detailed Spectra–Structure Correlations—Overlapping Spectra

FIGURE A3.18

FIGURE A3.19


Alkynes

Absorbance
Alkynes

FIGURE A3.20

Amides

1.0 - Acetamide, N-methyl, 98%
0.9 - Formamide, 98%

Absorbance

\[3vC-H\]
\[2\nu N-H\]
\[3\nu H-C=O\]


FIGURE A3.21
Amides

Acetamide, N-methyl-, 98%  
Formamide, 98%

$2\nu N-H$  
$2\nu C-H$

$\nu_{\text{NH}} + \delta_{\text{NH}}$ (Amide II)  
$2\nu \text{C}=\text{O}$ + Amide III

First Combination Region CH

Absorbance

Cm$^{-1}$  
Nm

7000 1429
6500 1538
6000 1667
5500 1818
5000 2000

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FIGURE A3.22
FIGURE A3.23

Carboxylic Acids

3νC-H

Ar-CH

CH₂

CH₃-COOH

CH (Formic)

Second Combination Region CH

Third Combination Region CH

2νO-H


Benzoic acid, anhydride, 98%
Dodecanoic acid, 99%
Formic acid, 98%
Acetic acid, 99%
Carboxylic Acids

Benzoic acid, anhydride, 98%
Decanoic acid, 98%
Formic acid, 98%
Acetic acid, 99%

First Combination Region CH

2νC-H

CH₂

CH₂

3νC=O

ν+δ O-H

Ar-CH

Sloping Baseline

OH


FIGURE A3.24
Alkyl Dienes

3νC-H

ν H-C=C*


FIGURE A3.25
Alkyl Dienes

**FIGURE A3.26**


FIGURE A3.27

Compound Type Comparison

3νC-H

Second Combination Region CH

2νO-H

1-Decanamine, 97%
2-Propanol, 2-methyl, 99.5%
3-Hexanone, 96%
Pentane, 2,2,4-trimethyl, 99%
Undecane, 99%
Benzene, methyl-, 99%

Abundance

FIGURE A3.28

Compound Type Comparison

FIGURE A3.29


First Combination Region CH

2vC-H

2vN-H

Ar-CH

CH$_3$

CH$_2$

CH$_3$ + HN

H$_2$O + OH

H$_3$N + HN

H$_2$N + HN

38N-H

FIGURE A3.30

Compound Type Comparison

2νC-H

First Combination Region CH

Benzene, methyl-, 99%
Pentane, 2,2,4-trimethyl-, 99%
Undecane, 99%
3-Hexanone, 96%
2-Propanone, 2-methyl-, 99.5%
1-Decanol, 97%

Absorbance

Cm⁻¹
Nm

7000 6500 6000 5500 5000 4500 4000
1429 1538 1667 1818 2000 2222 2500

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FIGURE A3.30
FIGURE A3.31

Third Overtone Compound Comparison

\[ 4\nu C-H \]

Appendix 4a: Spectra–Structure Correlations for Near Infrared (in Ascending Wavelength and Descending Wavenumber Order)*

<table>
<thead>
<tr>
<th>Nanometers (nm)</th>
<th>Wavenumbers (cm⁻¹)</th>
<th>Functional Group</th>
<th>Spectra–Structure</th>
<th>Material Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>513</td>
<td>19,500</td>
<td>O–H alkyl alcohols O–H with no hydrogen bonding (R–C–OH) in CCl₄</td>
<td>O–H (6v) from nonhydrogen-bonded short-chain alkyl alcohols in CCl₄ as (R–C–OH)</td>
<td>Alkyl alcohols</td>
</tr>
<tr>
<td>599</td>
<td>16,700</td>
<td>O–H alkyl alcohols O–H with no hydrogen bonding (R–C–OH) in CCl₄</td>
<td>O–H (5v) from nonhydrogen-bonded short-chain alkyl alcohols in CCl₄ as (R–C–OH)</td>
<td>Alkyl alcohols</td>
</tr>
<tr>
<td>714</td>
<td>13,986</td>
<td>C–H aromatic (ArCH)</td>
<td>C–H (5v), aromatic C–H</td>
<td>Hydrocarbons, aromatic</td>
</tr>
<tr>
<td>741</td>
<td>13,500</td>
<td>O–H alkyl alcohols O–H with no hydrogen bonding (R–C–OH) in CCl₄</td>
<td>O–H (4v) from nonhydrogen-bonded short-chain alkyl alcohols in CCl₄ as (R–C–OH)</td>
<td>Alkyl alcohols</td>
</tr>
<tr>
<td>747</td>
<td>13,387</td>
<td>C–H methyl C–H (CH₃)</td>
<td>C–H (5v), methyl C–H</td>
<td>Hydrocarbons, aliphatic</td>
</tr>
<tr>
<td>773</td>
<td>12,937</td>
<td>O–H from secondary alcohols as (–CH–OH)</td>
<td>O–H (4v) (–CH–OH), secondary alcohols</td>
<td>Secondary alcohols</td>
</tr>
<tr>
<td>796</td>
<td>12,563</td>
<td>C–H methyl C–H, associated with linear aliphatic CH₂(CH₃)₂, CH₃</td>
<td>C–H (4vCH₂ and δCH₂) combination</td>
<td>Hydrocarbons, aliphatic</td>
</tr>
<tr>
<td>803</td>
<td>12,453</td>
<td>C–H methyl C–H, associated with aromatic (ArCH₂)</td>
<td>C–H (4vCH₂ and δCH₂) combination</td>
<td>Hydrocarbons, aromatic</td>
</tr>
<tr>
<td>813</td>
<td>12,300</td>
<td>C–H methyl C–H, associated with branched aliphatic RC(CH₃)₂ or RCH(CH₃)₂</td>
<td>C–H (4vCH₂ and δCH₂) combination</td>
<td>Hydrocarbons, aliphatic</td>
</tr>
<tr>
<td>830</td>
<td>12,048</td>
<td>C–H methylene C–H, associated with linear aliphatic R(C)CH₂(R)</td>
<td>C–H (4vCH₂ and δCH₂) combination</td>
<td>Hydrocarbons, aliphatic</td>
</tr>
<tr>
<td>836</td>
<td>11,962</td>
<td>C–H methylene C–H, associated with branched aliphatic RC(CH₃)₂ or RCH(CH₃)₂</td>
<td>C–H (4vCH₂ and δCH₂) combination</td>
<td>Hydrocarbons, aliphatic</td>
</tr>
<tr>
<td>876</td>
<td>11,655</td>
<td>C–H aromatic (ArCH)</td>
<td>C–H (4v), aromatic C–H</td>
<td>Hydrocarbons, aromatic</td>
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<td>908</td>
<td>11,052</td>
<td>C–H methyl (CH₃)</td>
<td>C–H (4v), CH₃</td>
<td>Hydrocarbons, methyl</td>
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<td>915</td>
<td>10,929</td>
<td>C–H methyl C–H (CH₃)</td>
<td>C–H (4v), methyl C–H</td>
<td>Hydrocarbons, aliphatic</td>
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<tr>
<td>930</td>
<td>10,753</td>
<td>C–H methylene (CH₂)</td>
<td>C–H (4v), methylene C–H</td>
<td>Hydrocarbons, aliphatic</td>
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<td>930</td>
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<td>C–H methylene (CH₂)</td>
<td>C–H (4v), CH₂</td>
<td>Hydrocarbons, methylene</td>
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<tr>
<td>Wavenumber</td>
<td>Frequency</td>
<td>Description</td>
<td>Notes</td>
<td></td>
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<td>-----------</td>
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<td>-------</td>
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<tr>
<td>962</td>
<td>10,400</td>
<td>O–H alkyl alcohols O–H with no hydrogen bonding (R–C–OH) in CCl₄</td>
<td>Alkyl alcohols</td>
<td></td>
</tr>
<tr>
<td>990</td>
<td>9911 and 10,288 (doublet)</td>
<td>O–H phenols, dilute phenol in CCl₄</td>
<td>Phenolic O–H</td>
<td></td>
</tr>
<tr>
<td>996</td>
<td>10,040</td>
<td>O–H from primary alcohols as (–CH₂–OH)</td>
<td>Primary alcohols</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>10,000</td>
<td>O–H phenols, dilute phenol in CCl₄</td>
<td>Phenolic O–H</td>
<td></td>
</tr>
<tr>
<td>1003.0</td>
<td>9970</td>
<td>N–H primary aromatic amine (o-NO₂)</td>
<td>Aromatic amine</td>
<td></td>
</tr>
<tr>
<td>1004</td>
<td>9960</td>
<td>O–H from secondary alcohols as (–CH–OH)</td>
<td>Secondary alcohols</td>
<td></td>
</tr>
<tr>
<td>1006</td>
<td>9940</td>
<td>O–H from tertiary alcohols as (–C–OH)</td>
<td>Tertiary alcohols</td>
<td></td>
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<tr>
<td>1015.0</td>
<td>9852</td>
<td>N–H primary aromatic amine (m-NO₂)</td>
<td>Aromatic amine</td>
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<td>1017.5</td>
<td>9828</td>
<td>N–H primary aromatic amine (o-Cl)</td>
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</tr>
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<td>1018.5</td>
<td>9818</td>
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<td>1018.5</td>
<td>9818</td>
<td>N–H primary aromatic amine (o-OCH₃)</td>
<td>Aromatic amine</td>
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<tr>
<td>1019.0</td>
<td>9813</td>
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<td>1021</td>
<td>9796</td>
<td>C–H methyl C–H, associated with aromatic (ArCH₃)</td>
<td>Hydrocarbons, aromatic</td>
<td></td>
</tr>
<tr>
<td>1021</td>
<td>9794</td>
<td>C–H methyl C–H, associated with branched aliphatic RC(CH₃)₃ or RCH(CH₃)₂</td>
<td>Hydrocarbons, aliphatic</td>
<td></td>
</tr>
<tr>
<td>1021</td>
<td>9795</td>
<td>C–H methyl C–H, associated with linear aliphatic CH₃(CH₂)ₙ CH₃</td>
<td>Hydrocarbons, aliphatic</td>
<td></td>
</tr>
<tr>
<td>Nanometers (nm)</td>
<td>Wavenumbers (cm(^{-1}))</td>
<td>Functional Group</td>
<td>Spectra–Structure</td>
<td>Material Type</td>
</tr>
<tr>
<td>----------------</td>
<td>-----------------------------</td>
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<td>-------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>102.10</td>
<td>9794</td>
<td>N–H primary aromatic amine (no other substituents)</td>
<td>N–H (3(\nu)) asymmetric, primary aromatic amine in CCl(_4) no other substituents</td>
<td>Aromatic amine</td>
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<tr>
<td>102.30</td>
<td>9775</td>
<td>N–H primary aromatic amine (p-CH(_3))</td>
<td>N–H (3(\nu)) asymmetric, primary aromatic amine in CCl(_4) as para-CH(_3) grouping</td>
<td>Aromatic amine</td>
</tr>
<tr>
<td>102.65</td>
<td>9741</td>
<td>N–H primary aromatic amine (p-NH(_2))</td>
<td>N–H (3(\nu)) asymmetric, primary aromatic amine in CCl(_4) as para-NH(_2) grouping</td>
<td>Aromatic amine</td>
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<tr>
<td>102.9</td>
<td>9720</td>
<td>O–H/C–O polyfunctional alkyl alcohols</td>
<td>2(\nu)O–H and 3(\nu)C–O combination</td>
<td>Ethers and esters also containing alcohols</td>
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<tr>
<td>104.1</td>
<td>9606</td>
<td>C–H methylene C–H, associated with linear aliphatic R(CH(_2))(_n)R</td>
<td>C–H (3(\nu)CH(_3) and 3(\nu)CH(_2)) combination</td>
<td>Hydrocarbons, aliphatic</td>
</tr>
<tr>
<td>104.2</td>
<td>9600</td>
<td>C–H methylene C–H, associated with branched aliphatic R(CH(_2))(_n) or RCH(CH(_3))(_n)</td>
<td>C–H (3(\nu)CH(_3) and 3(\nu)CH(_2)) combination</td>
<td>Hydrocarbons, aliphatic</td>
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<tr>
<td>104.7</td>
<td>9550</td>
<td>O–H with hydrogen bonding (R–C–OH)</td>
<td>O–H (3(\nu)) from hydrogen-bonded short-chain alkyl compounds</td>
<td>Alkyl alcohols</td>
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<tr>
<td>106.5</td>
<td>9386</td>
<td>O–H combination band, alcohols or water</td>
<td>2(\nu)O–H and 3(\nu)C–H methyl combination</td>
<td>Alcohols as R–C–O–H combination</td>
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<td>114.2</td>
<td>8754</td>
<td>C–H aromatic (ArCH)</td>
<td>C–H (3(\nu)), aromatic C–H</td>
<td>Hydrocarbons, aromatic</td>
</tr>
<tr>
<td>114.3</td>
<td>8749</td>
<td>C–H (aromatic C–H)</td>
<td>C–H (3(\nu)), Ar.C–H</td>
<td>Hydrocarbons, aromatic</td>
</tr>
<tr>
<td>116.0</td>
<td>8621</td>
<td>C=O (carbonyl &gt;C=O)</td>
<td>C=O (5(\nu))</td>
<td>Hydrocarbons, aliphatic</td>
</tr>
<tr>
<td>117.0</td>
<td>8547</td>
<td>C–H alkene (HC=C=CH)</td>
<td>C–H (3(\nu)), HC=C=CH</td>
<td>Alkenes, polyenes</td>
</tr>
<tr>
<td>119.4</td>
<td>8375</td>
<td>C–H methyl C–H, (CH(_3))</td>
<td>C–H (3(\nu)), methyl C–H</td>
<td>Hydrocarbons, aliphatic</td>
</tr>
<tr>
<td>119.5</td>
<td>8368</td>
<td>C–H methyl (CH(_3))</td>
<td>C–H (3(\nu)), (CH(_3))</td>
<td>Hydrocarbons, aliphatic</td>
</tr>
<tr>
<td>121.1</td>
<td>8258</td>
<td>C–H methylene (CH(_2))</td>
<td>C–H (3(\nu)), methylene C–H</td>
<td>Hydrocarbons, aliphatic</td>
</tr>
<tr>
<td>121.5</td>
<td>8230</td>
<td>C–H methylene (CH(_2))</td>
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<td>C–H methyl C–H, associated with linear aliphatic CH(_3), CH(CH(_3))(_2), CH(_2)</td>
<td>C–H (2(\nu)CH(_2) and 3(\nu)CH(_2)) combination</td>
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<td>O–H alcohol (RO–H)</td>
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<td>O–H-bound water with several hydrogen bonds and the first overtone of an NH-stretching mode of the amide groups of ovalbumin</td>
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<td>N–H [bonded NH stretching and 2 × amide II deformation (N–H in-plane bending) combination] from polyamide 11</td>
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<td>O–H and δO–H combination reported in the literature from ethylene-vinyl alcohol copolymer spectra, probably better assigned as 2νO–H</td>
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<td>C–H vinyl C–H attached to &gt;C=O group, such as (CH(_2)=CH–C=O –)</td>
<td>C–H, vinyl on O (1-ethenyl-1-ethoxybutane as (CH(_2)=CH–C=O –))</td>
<td>Vinyl as 1-ethyl vinyl oxybutane (1-ethenyl-1-ethyl-ketone)</td>
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<td>N–H [4 × amide II (N–H in-plane bending)] from polyamide 11</td>
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<td>C–H (2ν), =CH(_2)</td>
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Spectra—Structure Correlations for Near Infrared

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<td>C–H methyl C–H, OH associated as ((\text{ROHCH}_3))</td>
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<td>5985 (5988)</td>
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<td>C–H aromatic C–H (aryl)</td>
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<td>C–H methyl C–H, carbonyl adjacent as ((\text{C=OCH}_3))</td>
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<td>5952</td>
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<td>C–H aromatic (ArCH)</td>
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<td>Reference — classic filter instrument</td>
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<td>C–H methyl C–H, carbonyl associated as one C removed ((\text{C=OCH}_3,\text{CH}_3))</td>
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<td>C–H aromatic C–H</td>
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<td>C–H methyl C–H, OH associated as ((\text{ROHCH}_3))</td>
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<td>C–H aromatic C–H (aryl)</td>
<td>CHv=CHv (15 + 5), benzene band assignment</td>
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<td>1693</td>
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<td>C–H methyl C–H branched</td>
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<td>C–H methyl, carbonyl associated as one C removed (C=OCH₂CH₃)</td>
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<td>Proteins (ArCH(_3))</td>
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<td>S–H thiol ((\cdot)S–H)</td>
<td>S–H ((\nu)), (\cdot)S–H</td>
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<td>C–H ((\nu)) from silicone</td>
<td>C–H ((\nu)) stretch from silicone</td>
<td>Silicone (dimethyl siloxane)</td>
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<td>1790</td>
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<td>O–H from water</td>
<td>O–H combination</td>
<td>Water</td>
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<td>1820</td>
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<td>O–H/(\cdot)C–H combination</td>
<td>O–H stretching and C–O stretching ((\nu_2)) combination</td>
<td>Cellulose</td>
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<td>1860</td>
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<td>C–Cl chlorinated organics ((\cdot)Cl group)</td>
<td>C–Cl ((\nu_7)), C–Cl</td>
<td>Chlorinated hydrocarbons</td>
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<td>1892</td>
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<td>O–H assigned as a one-to-one hydrogen bonded to an isolated OH in the manner as OH:OH(_2) from the effect of the hydration of the isolated alcohol OH — this pertains to the interactions of water with the OH groups in poly(ethylene-co-vinyl alcohol) (EVOH)</td>
<td>Water and polyvinyl alcohol OH</td>
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<td>C=O carbonyl ((\cdot)C=OOH)</td>
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<td>O–H (2ν), P=OH</td>
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<td>1920</td>
<td>5208</td>
<td>C=O amide (C=ONH)</td>
<td>C=O (3ν), C=ONH</td>
<td>Amide</td>
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<td>1923</td>
<td>5200</td>
<td>O–H assigned to molecular water [O–H (O–H and HOH)]</td>
<td>O–H assigned to molecular water (O–H stretching and HOH deformation combination)</td>
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<td>O–H (O–H and HOH)</td>
<td>O–H stretching and HOH deformation combination from water molecules in the 3-aminopropyltriethoxysilane-ethanol-water system</td>
<td>3-aminopropyltriethoxysilane-ethanol-water system</td>
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<td>O–H (O–H and HOH)</td>
<td>O–H stretching and HOH bending combination</td>
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<td>Si–O–H stretch + Si–O–Si deformation combination from silicone (dimethyl siloxane)</td>
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<td>Moisture (classic)</td>
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<td>O–H stretching and HOH bending combination</td>
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<td>Water and polyvinyl alcohol OH</td>
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<td>C=O (3ν), C=OOR</td>
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<td>O–H and CH combination from methanol</td>
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<td>N–H amide II (.CONH₂)</td>
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<td>N–H ((\nu)N–H and (\delta)N–H combination), primary aromatic amine in CCl(_4) as para-NH(_2) grouping</td>
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<td>N–H stretching and N–H bending combination</td>
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<td>N–H ammonia in water</td>
<td>N–H ((\nu)N–H and (\delta)N–H combination) for NH(_3) (ammonia) in water</td>
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<td>2010</td>
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<td>N–H/C–N combination band from primary amides (R–C=O–NH(_2))</td>
<td>N–H [(\nu)N–H symmetric and amide III deformation (C–N stretching/N–H in-plane bending) combination] for primary amides</td>
<td>Primary amides</td>
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<td>N–H/C=O combination from polyamide 11</td>
<td>N–H/C=O [bonded NH stretching and amide I (2(\nu)C=O stretching) combination] from polyamide 11</td>
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<td>(\nu)O–H and (\delta)O–H combination from CH(_3)OH</td>
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<td>N–H/C=O [bonded NH stretching and amide I (2(\nu)C=O stretching) combination] of native RNase A</td>
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Spectra—Structure Correlations for Near Infrared

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<td>2050 4878</td>
<td>N−H combination band (RNase A) − C=O amide I band</td>
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<td>2050 4878</td>
<td>N−H/C=O amide as (CONH₂) and (CONH₂) from native RNase A (thermal unfolding)</td>
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<td>2050 4878</td>
<td>N−H/C=N/N−H amide II and amide III combination (CONH₂) and (CONH₂)</td>
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<td>2053 4870</td>
<td>N−H combination from polyamide 11</td>
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<td>2053 4867–4878</td>
<td>N−H band found at 4867 cm⁻¹ for native RNase A shifting to 4878 cm⁻¹ upon thermal unfolding</td>
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<td>CONH₂ specifically due to peptide N−H and C=O groups at right angles to the line of the peptide backbone referred to as the β-sheet structure</td>
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<td>2055 4867</td>
<td>N−H combination band (RNase A) − C=O amide I band</td>
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<td>N−H from gamma-valerolactam</td>
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<td>2055 4866</td>
<td>N−H/C=O amide as (CONH₂) and (CONH₂)</td>
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<td>N–H/C=O amide as (CONH₂) and (CONH₂) from native RNase A</td>
<td>N–H stretching and C=O stretching (amide I) combination band in the spectrum of native RNase A</td>
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<td>HN...O=C band of amide A</td>
<td>CONH₂ combination of amide A and amide II</td>
<td>Proteins (polypeptides)</td>
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<td>N–H amide as (CONH₂) and (CONH₂)</td>
<td>N–H (δ) and N–H stretching combination</td>
<td>Amides/proteins</td>
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<td>N–H combination band from secondary amides in native RNase A</td>
<td>N–H [νN–H and amide II deformation (N–H in-plane bending) combination] for secondary amides in native RNase A</td>
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<td>O–H and C–O stretching and bending combination from methanol</td>
<td>νO–H and δO–H combination from CH₃OH</td>
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<td>5550–4550 (broad)</td>
<td>O–H broad band occurring in polyols, alcohols, water, ethylene vinyl alcohols and copolymers containing O–H groups</td>
<td>O–H broad band, due to νO–H and δO–H combination</td>
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<td>4800</td>
<td>O–H related combination from water change in phase and N–H/C–N combination band from urea (NH₂–C=O–NH₂) from ovalbumin</td>
<td>O–H related combination from water change in phase with the increase in protein concentration at pH above 2.8 overlapping with a band representing the N–H/C–N [νN–H asymmetric and amide III deformation (C–N stretching/N–H in-plane bending) combination]</td>
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<td>N–H from gamma-valerolactam</td>
<td>N–H [NH stretching and amide II deformation (N–H in-plane bending) combination] for gamma-valerolactam</td>
<td>Gamma-valerolactam</td>
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<td>O–H deformation band, alcohols or water</td>
<td>O–H combination</td>
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<td>C=O–O polymeric (C=O and C–O stretching)</td>
<td>C=O–O (4v)</td>
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<td>O–H/C–O stretching combination from methanol</td>
<td>νO–H and νC–O combination from CH$_3$OH</td>
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<td>N–H/C=O combination from polyamide 11</td>
<td>N–H/C=O (2 × amide II (N–H in-plane bending) and amide I (2νC=O stretching) combination) from polyamide 11</td>
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<td>C–H/C=O lipid associated (RC=CH and RC=O)</td>
<td>C–H stretching and C=O stretching combination and C–H deformation combination</td>
<td>Lipids</td>
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<td>2145</td>
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<td>N–H/C–N/C=O from gamma-valerolactam</td>
<td>N–H/C–N/C=O (2 × amide I (2νC=O stretching) and amide III deformation (C–N stretching/N–H in-plane bending) combination) for gamma-valerolactam</td>
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<th>Spectra–Structure</th>
<th>Material Type</th>
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<td>CONH₂ specifically due to C=O hydrogen bonded to the N–H of the peptide link termed the α-helix structure</td>
<td>CONH₂ specifically due to the α-helix peptide structure</td>
<td>Proteins as normalized 2nd-derivative spectra of proteins in aqueous solution</td>
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<td>4608</td>
<td>C–H alkenes (HC=CH)</td>
<td>C–H stretching and C–H deformation combination</td>
<td>Alkenes</td>
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<td>CONH₂ as combination of amide B and amide II modes (amide B/amide II) from ovalbumin</td>
<td>CONH₂ as combination of amide B and amide II modes (amide B/amide II)</td>
<td>Amides</td>
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<td>CONH₂ specifically due to amide B and amide II modes (amide B/II) from ovalbumin protein side chains seen at shifting to lower wavenumber with considerable broadening at lowered pH (from pH 5.0 to 2.4)</td>
<td>CONH₂ specifically due to amide B and amide II modes (amide B/II)</td>
<td>Proteins at low pH</td>
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<td>N–H proteins: N–H (3νₐ)</td>
<td>N–H (3)</td>
<td>Protein/amino acids</td>
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<td>N–H/C–N/C=O combination band from secondary amides in proteins</td>
<td>N–H/C–N/C=O [2 × amide I (2νC=O stretching) and amide III deformation (C–N stretching/N–H in-plane bending) combination] for secondary amides in proteins</td>
<td>Protein</td>
</tr>
<tr>
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<td>N–H/C–N/C=O combination band from urea (NH₂–C=O–NH₂)</td>
<td>N–H/C–N/C=O [2 × amide I (2νC=O stretching) and amide III deformation (C–N stretching/N–H in-plane bending) combination] for urea</td>
<td>Urea</td>
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<td>N–H/C–N/N–H combination from polyamide 11</td>
<td>N–H/C–N/N–H [bonded NH stretching and amide III (C–N stretching/N–H in-plane bending) combination] from polyamide 11</td>
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<td>C–H aromatic C–H (aryl)</td>
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<td>C–H aryl</td>
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<tr>
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<td>CHO carbohydrate (.CHO)</td>
<td>C–H stretching and C=O combination</td>
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<tr>
<td>2205</td>
<td>4535</td>
<td>N–H primary amine band of diamino-compound</td>
<td>N–H (3\nu) band of primary amine as bisphenol A (I) resins cured with 4,4'-diaminodiphenyl sulfone (II) hardener</td>
<td>Amine, primary</td>
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<tr>
<td>2206</td>
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<td>2207</td>
<td>4525–4540</td>
<td>CONH₂ specifically due to peptide N–H and C=O groups at right angles to the line of the peptide backbone referred to as the ( \beta )-sheet structure</td>
<td>Proteins as normalized 2nd-derivative spectra of proteins in aqueous solution</td>
<td></td>
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<tr>
<td>2210</td>
<td>4525</td>
<td>N–H ammonia in water</td>
<td>N–H (3\nu) for NH₃ (ammonia) in water</td>
<td>Ammonia in water</td>
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<td>2212</td>
<td>4521</td>
<td>C=O/C–( \nu )NN–H combination from polyamide 11</td>
<td>C=O/C–( \nu )NN–H [2 \times amide I (2\nuC=O stretching) and amide III (C–N stretching/N–H in-plane bending) combination] from polyamide 11</td>
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<td>4505</td>
<td>N–H combination band from urea (NH₂–C=O–NH₂)</td>
<td>N–H (( \nu )N–H asymmetric and NH₂ rocking) combination</td>
<td>N–H from urea</td>
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<td>4484</td>
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<td>Classic filter instrument</td>
<td>Reference (classic)</td>
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<td>4405</td>
<td>CHO — classic filter instrument</td>
<td>Classic filter instrument</td>
<td>Lignin</td>
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<td>Proteins as normalized 2nd-derivative spectra of proteins in aqueous solution</td>
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<td>2273</td>
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<td>O–H/C–O from glucose</td>
<td>O–H/C–O glucose absorption from O–H stretching and C–O stretching combination</td>
<td>Glucose</td>
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<td>C–H starch (.C–H and CH₃)</td>
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<td>CONH₂ specifically due to C=O hydrogen bonded to the N–H of the peptide link termed the ( \alpha )-helix structure</td>
<td>CONH₂ specifically due to the ( \alpha )-helix peptide structure</td>
<td>Proteins as normalized 2nd-derivative spectra of proteins in aqueous solution</td>
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<td>C–H (3δ) from silicone</td>
<td>C–H (3δ) bend from silicone (dimethyl siloxane)</td>
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<td>C–H (3δ)</td>
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<td>C–H (2νCH₃ asymmetric stretching and ťCH₃) combination</td>
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<td>407</td>
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<td>C–H stretching and CH₃ deformation combination</td>
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<tr>
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<td>C–H (C–H and CH₃)</td>
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<td>C–H methylene C–H, associated with ovalbumin protein side chains seen at pH 5.0</td>
<td>C–H (2νCH₃ symmetric stretching and ťCH₃) combination band from ovalbumin protein side chains seen at pH 5.0</td>
<td>C–H from ovalbumin protein side chains</td>
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<td>4261</td>
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<td>O–H from primary alcohols as (–CH–OH)</td>
<td>O–H (ν) (–CH₂–OH), primary alcohols</td>
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<td>CHν+CCδ (12 + 18), benzene band assignment</td>
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<td>O–H from secondary alcohols as (–CH–OH)</td>
<td>O–H (ν) (–CH–OH), secondary alcohols</td>
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<td>O–H from tertiary alcohols as (–C–OH)</td>
<td>O–H (ν) (–C–OH), tertiary alcohols</td>
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<td>CONH₂ (HN–O=C band) of amide A</td>
<td>CONH₂ as amide A for the polypeptides</td>
<td>Amide A from proteins (polypeptides)</td>
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<td>3280</td>
<td>O–H stretching vibration (ν) of water molecules in bound-water hydrogen-bonding in turquoise minerals</td>
<td>O–H (ν) (as intense and very broad band assigned to bound-water hydrogen-bonding in turquoise minerals from Arizona and Senegal with a formula of Cu(Al₁₆–x,Fex)₄(OH)₈·₄H₂O)</td>
<td>Minerals</td>
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<td>3260</td>
<td>O–H stretching vibration (ν) of water molecules in protein-water hydrogen bonding</td>
<td>O–H (ν) (as intense and very broad band assigned to protein-water hydrogen bonding)</td>
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</tr>
<tr>
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<td>2840</td>
<td>O–H stretching vibrations of water molecules in water-water hydrogen bonding</td>
<td>O–H as intense and very broad band assigned to water-water hydrogen bonding</td>
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ABBREVIATIONS AND SYMBOLS

(1ν)  *Fundamental* stretching vibrational absorption band
(2ν)  *First* overtone of fundamental stretching band
(3ν)  *Second* overtone of fundamental stretching band
(4ν)  *Third* overtone of fundamental stretching band
(5ν)  *Fourth* overtone of fundamental stretching band
(6ν)  *Fifth* overtone of fundamental stretching band

(1δ)  *Fundamental* bending vibrational absorption band
(2δ)  *First* overtone of fundamental bending band
(3δ)  *Second* overtone of fundamental bending band
(4δ)  *Third* overtone of fundamental bending band

(ω)  Deformation (rocking or wagging)

Appendix 4b: Spectra–Structure Correlations for Near-Infrared (in Ascending Alphabetical Functional Group Order)*

1446
1417
1685
1671
1689
2148
2154
2167

Cˇ H
CˇH
CˇH
Cˇ H
CˇH
CˇH
CˇH
CˇH

(ArCˇH)
C ˇH
C ˇH
CˇH (aryl)
CˇH (aryl)
CˇH (aryl)
CˇH (aryl)
CˇH (aryl)

1680

CˇH aromatic (ArCH)

aromatic
aromatic
aromatic
aromatic
aromatic
aromatic
aromatic
aromatic

1142

CˇH aromatic (ArCH)

8547
6173
4608
13,986

1170
1620
2170
714

5985
5920
4655
4642
4615

6916
7057
5935
(5988)
(5914)
(4675)
(4644)
(4625)

5952

8754

11,655

4307
4292
4283
4348
4329
4252
4049
5721
4357
8749
6169

2322
2330
2335
2300
2310
2352
2470
1748
2295
1143
1621

876

5376

Wavenumbers (cm−1)

1860

Nanometers (nm)

Hydrocarbons, aromatic
Hydrocarbons, aromatic
Hydrocarbons, aromatic
CˇH aryl
CˇH aryl
CˇH aryl
CˇH aryl
CˇH aryl

Hydrocarbons, aromatic

Hydrocarbons, aromatic

Hydrocarbons, aromatic

Alkenes, polyenes
Alkenes
Alkenes
Hydrocarbons, aromatic

Polysaccharides
Polysaccharides
Polysaccharides
Amides
Lipids
Polysaccharides
Lipids, aliphatic compounds
CˇH from silicone (dimethyl siloxane)
CˇH from silicone (dimethyl siloxane)
Hydrocarbons, aromatic
Acrylate

CˇH stretching and CH2 deformation combination
CˇH stretching and CH2 deformation combination
CˇH stretching and CH2 deformation combination
CˇH (3δ)
CˇH (3δ)
CˇH (3δ)
CˇH combination
CˇH (2ν) stretch from silicone (dimethyl siloxane)
CˇH (3δ) bend from silicone (dimethyl siloxane)
CˇH (3ν), Ar.CˇH
CˇH, combination of two stretching modes
CˇH (3ν), .HCﬁCH
CˇH (2ν), .ﬁCH2
CˇH stretching and CˇH deformation combination
CˇH (5ν), aromatic
Cˇ H
CˇH (4ν), aromatic
Cˇ H
CˇH (3ν), aromatic
Cˇ H
CˇH (2ν), aromatic
Cˇ H
CˇH combination, ArCˇH
CˇH combination, Ar.CˇH
CˇH (2ν), ArCˇH
CHν+CHν (12 + 1), benzene band assignment
CHν+CHν (15 + 5), benzene band assignment
CHν+CCν (15 + 9), benzene band assignment
CHν+CCν (12 + 16), benzene band assignment
CCν+CHν (16 + 5), benzene band assignment

Chlorinated hydrocarbons

Material Type

CˇCl (7ν), .CˇCl

Spectra-Structure

266

CˇH aromatic (ArCH)

CˇCl chlorinated organics
(.CˇCl group)
CˇH (.CˇH and CH2)
CˇH (.CˇH and CH2)
CˇH (.CˇH and CH2)
CˇH (.CˇH bending)
CˇH (.CˇH bending)
CˇH (.CˇH bending)
CˇH (.CH2)
CˇH (2ν) from silicone
CˇH (3δ) from silicone
CˇH (aromatic CˇH)
CˇH acrylate CˇH
as (CH2ﬁCHCOO−)
CˇH alkene (.HCﬁCH)
CˇH alkene, .ﬁCH2
CˇH alkenes (.HCﬁCH)
CˇH aromatic (ArCH)

Functional Group

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<tr>
<td>C-H aromatic</td>
<td>2188</td>
<td>C&gt;H bond vibrations (13 + 1), benzene band assignment</td>
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<tr>
<td>C-H aromatic</td>
<td>2206</td>
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<td>C-H aromatic</td>
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<td>C&gt;G bond vibrations (11 + 12), benzene band assignment</td>
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<td>C&gt;H bond vibrations (4 + 1), benzene band assignment</td>
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<td>C&gt;G bond vibrations (18 + 5), benzene band assignment</td>
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<td>C-H from vinyl group as (CH₂=CH⁻)</td>
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<td>C-H pendant vinyl group of the 1,2 unit for liquid carboxylated poly(acrylonitrile-co-butadiene) or nitrile rubber (NBR)</td>
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<th>Functional Group</th>
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<tr>
<td>C-H methyl .(CH₃)</td>
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<td>C-H as RCH₂CHR branched</td>
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<tr>
<th>Functional Group</th>
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<th>Wavenumbers (cm⁻¹)</th>
<th>Spectra-Structure</th>
<th>Material Type</th>
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<td>5765</td>
<td>C–H methyl, amine associated as RN(CH₃)₂</td>
<td>Amines</td>
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<td>C–H methyl C–H, aromatic associated (ArCH₃)</td>
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<td>12453</td>
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<td>7300</td>
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<td>12300</td>
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<td>7163</td>
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<td>5898</td>
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<td>(.C=OCH2CH3)</td>
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<td>5882 (gas phase)</td>
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<th>Spectra-Structure</th>
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<td>Nitro (CH₃) as (CH₃NO₂)</td>
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<td>71.68</td>
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<td>C−H vinyl C−H attached to N group, such as (CH₂=CH−N−C=O−C)</td>
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<td>C−H, vinyl on N (1-ethenyl 2-pyrrolidinone) as (CH₂=CH−N−C=O−C)</td>
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<td>C−H, vinyl (hexene), CH₂=CH−</td>
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<td>C−H vinylidene C−H, associated with (CH₂=C&lt;)</td>
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<td>C=O (4ν)</td>
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<td>C=O (3ν), C=ONH</td>
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<td>C=O (3ν), C=ONH₂</td>
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<td>C=O (3ν), C=OOH</td>
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<td>5128</td>
<td>C=O (3ν), C=OOR</td>
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<td>4521</td>
<td>C=O/C−N/N−H [2× amide I (2νC=O stretching) and amide III (C−N stretching/N−H in-plane bending) combination] from polyamide 11</td>
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<td>C=O/N−H combination from polyamide 11</td>
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<td>C=O/N−H [amide I (2νC=O stretching) and 3× amide II (N−H in-plane bending) combination] from polyamide 11</td>
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| C=O–O polymeric (C=O and C–O stretching) | 2100 | 4762 | C=O–O (4v) | Polysaccharides  
| CONH₂ (HN...O=C band) of amide A | 3030 | 3300 | CONH₂ as amide A for the polypeptides | Amide A from proteins (polypeptides)  
| CONH₂ as combination of amide B and amide II modes (amide B/amide II) from ovalbumin | 2174 | 4600 | CONH₂ as combination of amide B and amide II modes (amide B/amide II) | Combination of amide B and amide II modes (amide B/amide II)  
| CONH₂ specifically due to amide B and amide II modes (amide B/II) from ovalbumin protein side chains seen at shifting to lower wavenumber with considerable broadening at lowered pH (from pH 5.0 to 2.4) | 1738 | 5755 | CONH₂ specifically due to the α-helix peptide structure | Proteins at low pH  
| CONH₂ specifically due to C=O hydrogen bonded to the N–H of the peptide link termed the α-helix structure | 2167 | 4615 | CONH₂ specifically due to the α-helix peptide structure | Proteins as normalized 2nd-derivative spectra of proteins in aqueous solution  
| CONH₂ specifically due to C=O hydrogen bonded to the N–H of the peptide link termed the α-helix structure | 2290 | 4365–4370 | CONH₂ specifically due to the α-helix peptide structure | Proteins as normalized 2nd-derivative spectra of proteins in aqueous solution  
| CONH₂ specifically due to C=O hydrogen bonded to the N–H of the peptide link termed the α-helix structure | 2445 | 4090 | CONH₂ specifically due to the α-helix peptide structure | Proteins as normalized 2nd-derivative spectra of proteins in aqueous solution  
| CONH₂ specifically due to peptide N–H and C=O groups at right angles to the line of the peptide backbone referred to as the β-sheet structure | 1690 | 5915–5925 | CONH₂ specifically due to peptide β-sheet structures | Proteins as normalized 2nd-derivative spectra of proteins in aqueous solution  

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<tr>
<th>Functional Group</th>
<th>Nanometers (nm)</th>
<th>Wavenumbers (cm⁻¹)</th>
<th>Spectra-Structure</th>
<th>Material Type</th>
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<td>CONH₂ specifically due to peptide N–H and C=O groups at right angles to the line of the peptide backbone referred to as the β-sheet structure</td>
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<td>Combination of amide A and amide II from proteins (polypeptides)</td>
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<td>N–H (2ν) symmetric, primary aromatic amine in CCl₄ as ortho-OC₃ substituent</td>
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<td>N–H primary aromatic amine (m-Cl)</td>
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<tr>
<td>O–H from primary alcohols as ((-\text{CH}_2)–OH)</td>
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<td>6887</td>
<td>O–H (2ν) ((-\text{CH}_2)–OH), primary alcohols</td>
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<tr>
<td>O–H from primary alcohols as ((-\text{CH}-\text{OH}))</td>
<td>2740</td>
<td>3650</td>
<td>O–H (ν) ((-\text{CH}_2)–OH), primary alcohols</td>
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<tr>
<td>O–H from secondary alcohols as ((-\text{CH}-\text{OH}))</td>
<td>773</td>
<td>12,937</td>
<td>O–H (4ν) ((-\text{CH}-\text{OH})), secondary alcohols</td>
<td>Secondary alcohols</td>
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<tr>
<td>O–H from secondary alcohols as ((-\text{CH}-\text{OH}))</td>
<td>1004</td>
<td>9960</td>
<td>O–H (3ν) ((-\text{CH}-\text{OH})), secondary alcohols</td>
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<tr>
<td>O–H from secondary alcohols as ((-\text{CH}-\text{OH}))</td>
<td>1464</td>
<td>6831</td>
<td>O–H (2ν) ((-\text{CH}-\text{OH})), secondary alcohols</td>
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<td>O–H from secondary alcohols as ((-\text{CH}-\text{OH}))</td>
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<td>3620</td>
<td>O–H (ν) ((-\text{CH}-\text{OH})), secondary alcohols</td>
<td>Secondary alcohols</td>
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<td>O–H from sugar as crystalline sucrose</td>
<td>1441</td>
<td>6940</td>
<td>O–H (2ν) carbohydrates (C4 hydroxyl within a crystalline matrix)</td>
<td>Crystalline sucrose</td>
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<th>Functional Group</th>
<th>Nanometers (nm)</th>
<th>Wavenumbers (cm$^{-1}$)</th>
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<th>Material Type</th>
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<tr>
<td>O–H from tertiary alcohols as (–C–OH)</td>
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<td>12,887</td>
<td>O–H (4v) (–C–OH), tertiary alcohols</td>
<td>Tertiary alcohols</td>
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<td>O–H from tertiary alcohols as (–C–OH)</td>
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<td>9940</td>
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<td>O–H from tertiary alcohols as (–C–OH)</td>
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<td>O–H (2v) (–C–OH), tertiary alcohols</td>
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<td>O–H from tertiary alcohols as (–C–OH)</td>
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<td>3610</td>
<td>O–H (ν) (–C–OH), tertiary alcohols</td>
<td>Tertiary alcohols</td>
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<td>O–H from water</td>
<td>1790</td>
<td>5587</td>
<td>O–H combination</td>
<td>Water</td>
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<tr>
<td>O–H hydrogen bonding between water and exposed polyvinyl alcohol OH</td>
<td>1892</td>
<td>5285</td>
<td>O–H assigned as a one-to-one hydrogen-bonded to an isolated OH in the manner as OH::OH, from the effect of hydration of the isolated alcohol OH — this pertains to the interactions of water with the OH groups in poly(ethylene-co-vinyl alcohol) (EVOH)</td>
<td>Water and polyvinyl alcohol OH</td>
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<tr>
<td>O–H hydrogen bonding between water and exposed polyvinyl alcohol OH</td>
<td>1942</td>
<td>5150</td>
<td>O–H interaction of multiple hydrogen atoms from poly(ethylene-co-vinyl alcohol) (EVOH) bonded to surrounding associated OH groups (from water) without clustering</td>
<td>Water and polyvinyl alcohol OH</td>
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<td>O–H hydroxyl O–H free form (not hydrogen bonded)</td>
<td>1410</td>
<td>7090</td>
<td>O–H, free hydroxyl group in dilute CCl$_4$</td>
<td>O–H not hydrogen bonded</td>
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<td>O–H methanol O–H with hydrogen bonding</td>
<td>1408</td>
<td>7100</td>
<td>O–H (2v) from nonhydrogen-bonded methanol in CCl$_4$ as (CH$_3$–OH)</td>
<td>O–H from methanol (nonhydrogen bonded)</td>
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<tr>
<td>O–H methanol O–H with hydrogen bonding</td>
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<td>O–H (2v) from nonhydrogen-bonded methanol in CCl$_4$ as (CH$_3$–OH)</td>
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<td>O–H phenolic O–H</td>
<td>1401–1441</td>
<td>7140–6940</td>
<td>2O–H from phenols and aryl alcohols Ar–OH</td>
<td>Phenolic O–H</td>
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<td>O–H phenols, dilute phenol in CCl$_4$</td>
<td>746 and 782</td>
<td>13,400 and 12,788 (doublet)</td>
<td>4O–H, ortho-iodophenol</td>
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<td>O–H phenols, dilute phenol in CCl$_4$</td>
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<td>13,250</td>
<td>4O–H dilute phenol in CCl$_4$</td>
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<td>O–H phenols, dilute phenol in CCl$_4$</td>
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<td>12,788 and 13,400 (doublet)</td>
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<td>O–H phenols, dilute phenol in $\text{CCl}_4$</td>
<td>1000 and 9720</td>
<td>9911 and 10,288 (doublet)</td>
<td>3νO–H dilute phenol in $\text{CCl}_4$</td>
<td>Phenolic O–H</td>
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<tr>
<td>O–H phenols, dilute phenol in $\text{CCl}_4$</td>
<td>1009 and 9720</td>
<td>9911 and 10,288 (doublet)</td>
<td>3νO–H, ortho-iodophenol</td>
<td>Phenolic O–H</td>
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<td>O–H phenols, ortho-substituted halogens</td>
<td>1464 and 6830</td>
<td>1464 and 6830</td>
<td>2νO–H in ortho-substituted halogens on phenols</td>
<td>Phenolic O–H</td>
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<td>O–H polymeric (.O–H)</td>
<td>1450 and 6897</td>
<td>1450 and 6897</td>
<td>O–H (2v), O–H</td>
<td>Starch/polymeric alcohol</td>
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<td>O–H polymeric (.O–H)</td>
<td>1490 and 6711</td>
<td>1490 and 6711</td>
<td>O–H (2v), O–H</td>
<td>Starch/polymeric alcohol</td>
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<tr>
<td>O–H polymeric (.O–H)</td>
<td>1540 and 6494</td>
<td>1540 and 6494</td>
<td>O–H (2v), O–H</td>
<td>Starch/polymeric alcohol</td>
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<tr>
<td>O–H related combination from water change in phase and N–H/C–N combination band from urea (NH$_2$–C=O–NH$_2$) from ovalbumin</td>
<td>2083 and 4800</td>
<td>2083 and 4800</td>
<td>O–H related combination from water change in phase with the increase in protein concentration at pH above 2.8 overlapping with a band representing the N–H/C–N [v$_3$N–H asymmetric and amide III deformation (C–N stretching/N–H in-plane bending) combination]</td>
<td>O–H related combination from water change in phase and N–H/C–N from ovalbumin protein</td>
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<tr>
<td>O–H stretching and bending combination from methanol</td>
<td>2016 and 4960</td>
<td>2016 and 4960</td>
<td>v O–H and δO–H combination from CH$_3$OH</td>
<td>Methanol O–H</td>
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<tr>
<td>O–H stretching vibration (ν) of water molecules in bound-water hydrogen bonding in turquoise minerals</td>
<td>3049 and 3280</td>
<td>3049 and 3280</td>
<td>O–H ν (as intense and very broad band assigned to bound-water hydrogen bonding in turquoise minerals from Arizona and Senegal with a formula of Cu(A16-χ,Fex)(PO4)4(4OH)8.4H$_2$O</td>
<td>Bound-water hydrogen bonding in minerals</td>
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<td>O–H stretching vibration (ν) of water molecules in protein-water hydrogen bonding</td>
<td>3067 and 3260</td>
<td>3067 and 3260</td>
<td>O–H as intense and very broad band assigned to protein-water hydrogen bonding</td>
<td>Protein-water hydrogen bonding</td>
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<tr>
<td>O–H stretching vibrations of water molecules in water-water hydrogen bonding</td>
<td>3521 and 2840</td>
<td>3521 and 2840</td>
<td>O–H as intense and very broad band assigned to water-water hydrogen bonding</td>
<td>Water-water hydrogen bonding</td>
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<tr>
<td>O–H with hydrogen bonding (R–C–OH)</td>
<td>1047 and 9550</td>
<td>1047 and 9550</td>
<td>O–H (3v) from hydrogen-bonded short-chain alkyl compounds</td>
<td>Alkyl alcohols</td>
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<tr>
<td>O–H, monomeric phenol in $\text{CCl}_4$</td>
<td>1420 and 7040</td>
<td>1420 and 7040</td>
<td>2νO–H monomeric phenol in $\text{CCl}_4$</td>
<td>Phenolic O–H</td>
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<tr>
<td>O–H/C–H combination</td>
<td>1820 and 5495</td>
<td>1820 and 5495</td>
<td>O–H stretching and C–O stretching (3v$_3$) combination</td>
<td>Cellulose</td>
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<tr>
<th>Functional Group</th>
<th>Nanometers (nm)</th>
<th>Wavenumbers (cm⁻¹)</th>
<th>Spectra-Structure</th>
<th>Material Type</th>
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<tr>
<td>O–H/C–O from glucose</td>
<td>2273</td>
<td>4400</td>
<td>O–H/C–O glucose absorption from O–H stretching and C–O stretching combination</td>
<td>Glucose</td>
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<td>O–H/C–O polyfunctional alkyl alcohols</td>
<td>1029</td>
<td>9720</td>
<td>2νO–H and 3νC–O combination</td>
<td>Ethers and esters also containing alcohols</td>
</tr>
<tr>
<td>O–H/C–O polymeric (O–H and C–O)</td>
<td>2100</td>
<td>4762</td>
<td>O–H bending and C–O stretching combination</td>
<td>Polysaccharides</td>
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<tr>
<td>O–H/C–O stretching combination from methanol</td>
<td>2123</td>
<td>4710</td>
<td>νO–H and νC–O combination from CH₃OH</td>
<td>Methanol O–H</td>
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<td>P–OH phosphate (P–OH)</td>
<td>1908</td>
<td>5241</td>
<td>O–H (2ν), P–OH</td>
<td>Phosphate</td>
</tr>
<tr>
<td>Reference — classic filter instrument</td>
<td>1680</td>
<td>5952</td>
<td>CH – aromatic used as classic reference filter for filter instruments</td>
<td>Reference (classic)</td>
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<tr>
<td>S–H thiol (S–H)</td>
<td>1740</td>
<td>5747</td>
<td>S–H (2ν), S–H</td>
<td>Thiols</td>
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<td>Si–O from silicone</td>
<td>1452</td>
<td>6887</td>
<td>Si–O (2ν) stretch from silicone (dimethyl siloxane)</td>
<td>Si–O from silicone (dimethyl siloxane)</td>
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<tr>
<td>Si–O–H stretch + Si–O–Si combination from silicone</td>
<td>1933</td>
<td>5173</td>
<td>Si–O–H stretch + Si–O–Si deformation combination from silicone (dimethyl siloxane)</td>
<td>Si–O–H stretch + Si–O–Si from silicone (dimethyl siloxane)</td>
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</table>
ABBREVIATIONS AND SYMBOLS

(1\nu) \textit{Fundamental} stretching vibrational absorption band
(2\nu) \textit{First} overtone of fundamental stretching band
(3\nu) \textit{Second} overtone of fundamental stretching band
(4\nu) \textit{Third} overtone of fundamental stretching band
(5\nu) \textit{Fourth} overtone of fundamental stretching band
(6\nu) \textit{Fifth} overtone of fundamental stretching band

(1\delta) \textit{Fundamental} bending vibrational absorption band
(2\delta) \textit{First} overtone of fundamental bending band
(3\delta) \textit{Second} overtone of fundamental bending band
(4\delta) \textit{Third} overtone of fundamental bending band

(\omega) Deformation (rocking or wagging)
Appendix 5: Spectra Index by Functional Group or Comparison Series Group
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<tr>
<th>Functional Group</th>
<th>Compound Name</th>
<th>Molecular Formula</th>
<th>CAS Number</th>
<th>10,500 – 6300 cm⁻¹ (952 – 1587 nm)</th>
<th>7200-3800 cm⁻¹ (1309 – 2632 nm)</th>
<th>Other NIR Regions</th>
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<tbody>
<tr>
<td>Alcohol (mono-OH)</td>
<td>1-Butanol</td>
<td>C₄H₁₀O</td>
<td>71-36-3</td>
<td>119, 208, 209</td>
<td>167, 210</td>
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</tr>
<tr>
<td>Alcohol (mono-OH)</td>
<td>1-Propanol</td>
<td>C₃H₇O</td>
<td>71-23-8</td>
<td>119, 209</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Alcohol (mono-OH)</td>
<td>2-Butanol</td>
<td>C₄H₁₀O</td>
<td>78-92-2</td>
<td>209</td>
<td>—</td>
<td>—</td>
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<tr>
<td>Alcohol (mono-OH)</td>
<td>2-methyl-2-Propanol</td>
<td>C₄H₁₀O</td>
<td>75-65-0</td>
<td>118, 119, 209, 234, 235</td>
<td>166, 167, 236, 237</td>
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<tr>
<td>Alcohol (mono-OH)</td>
<td>2-Propanol</td>
<td>C₃H₇O</td>
<td>67-63-0</td>
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<td>167</td>
<td>—</td>
</tr>
<tr>
<td>Alcohol (mono-OH)</td>
<td>3-Pentanol</td>
<td>C₅H₁₂O</td>
<td>584-02-01</td>
<td>119, 209</td>
<td>167</td>
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<tr>
<td>Alcohol (mono-OH)</td>
<td>Methanol</td>
<td>C₄H₈O</td>
<td>67-56-1</td>
<td>119, 208, 209</td>
<td>167, 210</td>
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<tr>
<td>Alcohol (diol)</td>
<td>1,2-Ethanediol</td>
<td>C₆H₁₂O</td>
<td>107-21-1</td>
<td>120</td>
<td>168</td>
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<tr>
<td>Alcohol (diol)</td>
<td>1,2-Propanediol</td>
<td>C₆H₁₂O</td>
<td>57-55-6</td>
<td>120</td>
<td>168</td>
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<tr>
<td>Alcohol (diol)</td>
<td>2,3-Butanediol</td>
<td>C₆H₁₂O</td>
<td>513-85-9</td>
<td>120, 210</td>
<td>168, 211</td>
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<tr>
<td>Alcohol (diol)</td>
<td>2,4-Pentanediol</td>
<td>C₆H₁₂O</td>
<td>625-69-4</td>
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<td>Alcohol (diol)</td>
<td>2,5-Hexanediol</td>
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<td>Butanediol Series</td>
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<td>Butanediol Series</td>
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<td>C₆H₁₂O</td>
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<td>169, 211</td>
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<td>Butanediol Series</td>
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<td>Ether</td>
<td>1,1,2-trimethoxy-Ethane</td>
<td>C₆H₁₂O</td>
<td>24332-20-5</td>
<td>122, 212</td>
<td>170, 213</td>
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<td>Ether</td>
<td>1,1-dimethoxy-Ethane</td>
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<td>534-15-6</td>
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<td>Ether</td>
<td>2-ethoxy-Ethanol</td>
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<td>110-80-5</td>
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<td>Ether</td>
<td>2-phenoxy-Ethanol</td>
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<td>122-99-6</td>
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<td>ethoxy-Acetic acid</td>
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<td>ethoxy-Ethyne</td>
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<td>Ether</td>
<td>ethoxy-Ethene</td>
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<td>2-Pentanol</td>
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<td>6032-29-7</td>
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<td>Pentanol Series</td>
<td>Cyclopentanol</td>
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<td>Pentanol Series</td>
<td>2-Butene-1,4-diol</td>
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<td>110-64-5</td>
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<td>172</td>
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<td>Pentanol Series</td>
<td>2-Propene-1-ol</td>
<td>C₂H₄O</td>
<td>107-18-6</td>
<td>124</td>
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<td>2-Propynal</td>
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<td>Butanal</td>
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<td>60% polypropylene-polyethylene acopolymer and 40% polyester</td>
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<td>Polypropylene, isotactic, chlorinated</td>
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<td>Cellulose acetate</td>
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<td>Cellulose acetate butyrate</td>
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<tr>
<td>Poly(vinylidene fluoride)</td>
<td>polymer</td>
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</table>

(continued)
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<th>Functional Group</th>
<th>Compound Name</th>
<th>Molecular Formula</th>
<th>CAS Number</th>
<th>10,500 – 6300 cm(^{-1}) (952 – 1587 nm)</th>
<th>7200-3800 cm(^{-1}) (1309 – 2632 nm)</th>
<th>Other NIR Regions</th>
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<tr>
<td>Polymers and Rubbers</td>
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<td>Poly(vinyl butyral) polymer</td>
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<tr>
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<td>Poly(vinyl chloride) polymer</td>
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<td>Poly(vinyl pyrrolidone) polymer</td>
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<td>Third Overtone C-H Comparison</td>
<td>Toluene</td>
<td>C(_7)H(_8)</td>
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<td>163, 238</td>
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<td>Third Overtone C-H Comparison</td>
<td>Trimethyl pentane</td>
<td>C(<em>3)H(</em>{18})</td>
<td>540-84-1</td>
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<td>Third Overtone C-H Comparison</td>
<td>n-Decane</td>
<td>C(<em>9)H(</em>{22})</td>
<td>124-18-5</td>
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<td>Third Overtone C-H Comparison</td>
<td>Acetone</td>
<td>C(_3)C(_6)O</td>
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<td>163, 238</td>
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<td>Third Overtone C-H Comparison</td>
<td>tert-Butanol</td>
<td>C(_4)H(_9)O</td>
<td>75-65-0</td>
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<td>163, 238</td>
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</table>

*Note: N/A indicates natural or synthetic product with no designated CAS number.*
Appendix 6: Spectra Index
by Alphanumerical Order
of Compound Name
<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Compound Name</th>
<th>Molecular Formula</th>
<th>CAS Number</th>
<th>10,500 – 6300 cm⁻¹ (952 – 1587 nm)</th>
<th>7200-3800 cm⁻¹ (1309 – 2632 nm)</th>
<th>Other NIR Regions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl (C₂) Comparison Group</td>
<td>1,1,1-trichloro-Ethane</td>
<td>C₃H₇Cl₃</td>
<td>71-55-6</td>
<td>133</td>
<td>181</td>
<td>—</td>
</tr>
<tr>
<td>Ether</td>
<td>1,1,2-trimethoxy-Ethane</td>
<td>C₄H₁₀O₃</td>
<td>24332-20-5</td>
<td>122, 212</td>
<td>170, 213</td>
<td>—</td>
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<tr>
<td>Aromatic (Aryl) Compound</td>
<td>1,1-Biphenyl</td>
<td>C₁₂H₁₀</td>
<td>92-52-4</td>
<td>150</td>
<td>198</td>
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<tr>
<td>Ether</td>
<td>1,1-dimethoxy-Ethane</td>
<td>C₄H₁₀O₂</td>
<td>534-15-6</td>
<td>122</td>
<td>170</td>
<td>—</td>
</tr>
<tr>
<td>Alcohol (diol)</td>
<td>1,2 Propanediol</td>
<td>C₃H₆O₂</td>
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<tr>
<td>Butanediol Seres</td>
<td>1,2-Butanediol</td>
<td>C₄H₁₀O₂</td>
<td>584-03-2</td>
<td>121</td>
<td>169, 211</td>
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<tr>
<td>Ethyl (C₂) Comparison Group</td>
<td>1,2-dibromo-Ethane</td>
<td>C₂H₄Br₂</td>
<td>106-93-4</td>
<td>133</td>
<td>181</td>
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<tr>
<td>Ethyl (C₂)</td>
<td>1,2-dichloro-Ethane</td>
<td>C₂H₄Cl₂</td>
<td>107-06-2</td>
<td>133</td>
<td>181</td>
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<tr>
<td>Ether</td>
<td>1,2-dimethoxy-Ethane</td>
<td>C₂H₆O₂</td>
<td>629-14-1</td>
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<td>170</td>
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<tr>
<td>Aromatic (Aryl) Compound</td>
<td>1,2-dimethyl-Benzene (xylene)</td>
<td>C₈H₁₀</td>
<td>95-47-6</td>
<td>150</td>
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<td>Alcohol (diol)</td>
<td>1,2-Ethanediol</td>
<td>C₂H₆O₂</td>
<td>107-21-1</td>
<td>120</td>
<td>168</td>
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<tr>
<td>Alkyl Amine</td>
<td>1,2-Propanediamine</td>
<td>C₄H₁₀N₂</td>
<td>78-90-0</td>
<td>142, 224</td>
<td>190, 225</td>
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<tr>
<td>Polyene</td>
<td>1,3,5-Cycloheptatriene</td>
<td>C₇H₈</td>
<td>544-25-2</td>
<td>158</td>
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<td>Butanediol Seres</td>
<td>1,3-Butanediol</td>
<td>C₄H₁₀O₂</td>
<td>107-88-0</td>
<td>121</td>
<td>169, 211</td>
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<td>Polyene</td>
<td>1,3-Cyclohexadiene</td>
<td>C₆H₁₂</td>
<td>592-57-4</td>
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<td>Polyene</td>
<td>1,3-Cyclooctadiene</td>
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<td>Butanediol Seres</td>
<td>1,4-Butanediol</td>
<td>C₄H₁₀O₂</td>
<td>110-63-4</td>
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<td>Aromatic (Aryl) Compound</td>
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<td>Polyene</td>
<td>1,5-Hexadiene</td>
<td>C₆H₁₂</td>
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<td>Alkyl Amine</td>
<td>1,7-Heptanediamine</td>
<td>C₇H₁₄N₂</td>
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<tr>
<td>Aryl versus Alkyl Series</td>
<td>1,7-Octadiene</td>
<td>C₈H₁₄</td>
<td>3710-30-3</td>
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<td>196</td>
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<td>Polyene</td>
<td>1,7-Octadiene</td>
<td>C₈H₁₄</td>
<td>3710-30-3</td>
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<td>X-H Compound Comparison</td>
<td>1-Butanamine (C-NH)</td>
<td>C₄H₉N</td>
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<td>Alcohol (mono-OH)</td>
<td>1-Butanol</td>
<td>C₄H₉O</td>
<td>71-36-3</td>
<td>119, 208, 209</td>
<td>167, 210</td>
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<td>Butyl Comparison Group</td>
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<td>71-36-3</td>
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<td>179</td>
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<td>Butyl Comparison Group</td>
<td>1-chlorobutane</td>
<td>C₄H₉Cl</td>
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<td>Propyl Comparison Group</td>
<td>1-chloro-Propane</td>
<td>C₄H₉Cl</td>
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<td>Alkyl Amine</td>
<td>1-Decanamine</td>
<td>C₁₀H₂₁N</td>
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<td>118, 142, 224, 234, 235</td>
<td>166, 190, 225, 236, 237</td>
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<td>157, 234</td>
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<td>Alkene</td>
<td>1-Decene</td>
<td>C₁₀H₁₆</td>
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<td>Alkene</td>
<td>1-Heptene</td>
<td>C(<em>{7})H(</em>{14})</td>
<td>592-76-7</td>
<td>222</td>
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<tr>
<td>Alkyne</td>
<td>1-Heptyne</td>
<td>C(<em>{7})H(</em>{12})</td>
<td>628-71-7</td>
<td>226</td>
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<tr>
<td>Alkene</td>
<td>1-Hexene</td>
<td>C(<em>{6})H(</em>{12})</td>
<td>592-41-6</td>
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<td>185</td>
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<td>120-72-9</td>
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<tr>
<td>Aromatic Compound with N or S</td>
<td>1-methyl-1H-Pyrrole</td>
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<td>195</td>
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<tr>
<td>Heterocyclic Compound</td>
<td>1-methyl-1H-Pyrrole</td>
<td>C(<em>{7})H(</em>{11})N</td>
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<tr>
<td>Alkene</td>
<td>1-Nonene</td>
<td>C(<em>{7})H(</em>{15})</td>
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<td>Alkene</td>
<td>1-Octene</td>
<td>C(<em>{8})H(</em>{16})</td>
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<td>Alkyne</td>
<td>1-Octyne</td>
<td>C(<em>{8})H(</em>{14})</td>
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<td>140, 226</td>
<td>188, 227</td>
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<td>Pentanol Series</td>
<td>1-Pentanol</td>
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<td>172</td>
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<td>Alkene</td>
<td>1-Pentene</td>
<td>C(<em>{5})H(</em>{10})</td>
<td>109-67-1</td>
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<td>185</td>
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<td>Alkyne</td>
<td>1-Pentyne</td>
<td>C(<em>{5})H(</em>{12})</td>
<td>627-19-0</td>
<td>140, 226</td>
<td>188, 227</td>
<td></td>
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<tr>
<td>Alcohol (mono-OH)</td>
<td>1-Propanol</td>
<td>C(<em>{5})H(</em>{10})O</td>
<td>71-23-8</td>
<td>119, 209</td>
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<tr>
<td>Propyl Comparison Group</td>
<td>1-Propanol</td>
<td>C(<em>{5})H(</em>{12})O</td>
<td>71-23-8</td>
<td>136</td>
<td>184</td>
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<tr>
<td>Acid vs. Amide vs. Ester Comparison</td>
<td>1-Propan-2-ol acetate</td>
<td>C(<em>{5})H(</em>{12})O (_{2})</td>
<td>108-22-5</td>
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<tr>
<td>Alkene</td>
<td>1-Tetradecene</td>
<td>C(<em>{14})H(</em>{28})</td>
<td>110-36-1</td>
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<td>185</td>
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<tr>
<td>Isomerism Comparison Group</td>
<td>2,2,4-trimethylpentane</td>
<td>C(<em>{12})H(</em>{26})</td>
<td>540-84-1</td>
<td>134</td>
<td>182</td>
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<tr>
<td>Aryl versus Alkyl Series</td>
<td>2,2,4-trimethyl-Pentane</td>
<td>C(<em>{12})H(</em>{26})</td>
<td>540-84-1</td>
<td>118, 148, 218, 219, 234, 235</td>
<td>166, 196, 220, 221, 236, 237</td>
<td></td>
</tr>
<tr>
<td>Functional Group Comparisons</td>
<td>2,2,4-trimethyl-Pentane</td>
<td>C(<em>{12})H(</em>{26})</td>
<td>540-84-1</td>
<td>157</td>
<td>205</td>
<td></td>
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<tr>
<td>Ether</td>
<td>2,2-dimethoxy-Propane</td>
<td>C(<em>{8})H(</em>{14})O (_{2})</td>
<td>77-76-7</td>
<td>122, 212</td>
<td>170, 213</td>
<td></td>
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<tr>
<td>Heterocyclic (5-member ring)</td>
<td>2,2-dimethyl-Thiazolidine</td>
<td>C(<em>{6})H(</em>{11})NS</td>
<td>19351-18-9</td>
<td>156</td>
<td>204</td>
<td></td>
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<tr>
<td>Alcohol (diol)</td>
<td>2,3-Butanediol</td>
<td>C(<em>{4})H(</em>{10})O (_{2})</td>
<td>513-85-9</td>
<td>120, 210</td>
<td>168, 211</td>
<td></td>
</tr>
<tr>
<td>Butanediol Series</td>
<td>2,3-Butanediol</td>
<td>C(<em>{4})H(</em>{10})O (_{2})</td>
<td>513-85-9</td>
<td>121, 208</td>
<td>169</td>
<td></td>
</tr>
<tr>
<td>Alkene, Internal versus Terminal</td>
<td>2,3-dimethyl-2-Butene</td>
<td>C(<em>{5})H(</em>{12})</td>
<td>563-79-1</td>
<td>139</td>
<td>187</td>
<td></td>
</tr>
<tr>
<td>Aromatic (Aryl) Compound</td>
<td>2,4,5-trichloro-Phenol</td>
<td>C(<em>{7})H(</em>{5})Cl(_{3})O</td>
<td>95-95-4</td>
<td>150</td>
<td>198</td>
<td></td>
</tr>
<tr>
<td>Aldehyde, Substituted Aromatic</td>
<td>2,4,6-trimethyl-Benzaldehyde</td>
<td>C(<em>{8})H(</em>{14})O (_{3})</td>
<td>487-68-3</td>
<td>129</td>
<td>177</td>
<td></td>
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<tr>
<td>Aldehyde, Substituted Aromatic</td>
<td>2,4-dimethyl-Benzaldehyde</td>
<td>C(<em>{8})H(</em>{14})O</td>
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<td>2,4-Pentanediol</td>
<td>C(<em>{5})H(</em>{14})O (_{2})</td>
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<td>Alcohol (diol)</td>
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<td>Aldehyde, Substituted Aromatic</td>
<td>2-bromo-Benzaldehyde</td>
<td>C(<em>{9})H(</em>{14})BrO</td>
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<td>2-bromo-Butane</td>
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<td>Ethyl (C(_{2})) Comparison Group</td>
<td>2-bromo-Ethanol</td>
<td>C(<em>{7})H(</em>{15})BrO</td>
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<td>2-bromo-Pyridine</td>
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<td>X-H Compound Comparison</td>
<td>2-Butanethiol (C-SH)</td>
<td>C(<em>{5})H(</em>{12})S</td>
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<th>7200-3800 cm⁻¹ (1309 – 2632 nm)</th>
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<td>Polyfunctional Comparison</td>
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<td>Cyclic Ether</td>
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<td>4-Octyne</td>
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<td>Acetic acid</td>
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<td>Benzaldehyde</td>
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<td>Benzenamine</td>
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<td>Aldehyde</td>
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<td>C₅H₁₀O</td>
<td>123-72-8</td>
<td>125, 216</td>
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<td>Four-Carbon (Butyl) Comparison</td>
<td>Butanoic Acid</td>
<td>C₅H₁₂O</td>
<td>107-92-6</td>
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<td>Polymers and Rubbers</td>
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<td>polymer</td>
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<td>Polymers and Rubbers</td>
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<td>Alkyl Amine</td>
<td>Cyclohexanamine</td>
<td>C₁₀H₁₄N</td>
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<td>Alkane &amp; Cycloalkane Comparison</td>
<td>Cyclohexane</td>
<td>C₆H₁₂</td>
<td>291-64-5</td>
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<td>Cyclohexene</td>
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<td>196, 220, 221</td>
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<td>Decanal</td>
<td>C₅H₁₀O₂</td>
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<td>Decanoic acid</td>
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<td>Molecular Formula</td>
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<td>Carboxylic Acid Dodecanoic acid</td>
<td>C_{12}H_{24}O_{2}</td>
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<td>306</td>
<td>Amino Acid D-Valine, 3-methyl, 1,1-dimethylethyl ester</td>
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<td>61169-85-5</td>
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<td>Ether ethoxy-Acetic acid</td>
<td>C_{4}H_{8}O_{3}</td>
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<td>Methyl Comparison Group Formic acid, methyl ester</td>
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<td>Cyclic Ether Furan</td>
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<td>Heterocyclic Compound Furan</td>
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<td>317</td>
<td>Aldehyde Heptanal</td>
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<td>319</td>
<td>Aryl Amine Indole, 1H</td>
<td>C_{8}H_{7}N</td>
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<td>194</td>
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<td>320</td>
<td>Aromatic Compound with N or S Indole, 1H-</td>
<td>C_{8}H_{7}N</td>
<td>120-72-9</td>
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<td>194</td>
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<td>Amino Acid L-Valine, 3-methyl, 1,1-dimethylethyl ester</td>
<td>C_{10}H_{21}NO_{2}</td>
<td>31556-74-8</td>
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<td>322</td>
<td>Alcohol (mono-OH) Methanol</td>
<td>CH_{4}O</td>
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<td>324</td>
<td>Ether methoxy-Benzene</td>
<td>C_{7}H_{8}O</td>
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<td>Carboxylic Acid Methyl ester-Benzoic acid</td>
<td>C_{8}H_{8}O_{2}</td>
<td>93-58-3</td>
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<td>326</td>
<td>Arom. Compound with N or S Methyl ester-Benzene</td>
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<td>327</td>
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<td>Functional Group Comparisons Methyl ester-Benzene</td>
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<td>329</td>
<td>Alkane Methylcyclopentane</td>
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<td>Aromatic Acid methyl-Benzene</td>
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<td>331</td>
<td>Aromatic Acid methyl-Benzene</td>
<td>CH_{4}</td>
<td>108-88-3</td>
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<td>332</td>
<td>Aromatic Acid methyl-Benzene</td>
<td>CH_{4}</td>
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<td>Functional Group</td>
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<td>Molecular Formula</td>
<td>CAS Number</td>
<td>10,500 – 6300 cm(^{-1}) (952 – 1587 nm)</td>
<td>7200-3800 cm(^{-1}) (1389 – 2632 nm)</td>
<td>Other NIR Regions</td>
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<td>Alkane &amp; Cycloalkane Comparison</td>
<td>methyl-Cyclopentane</td>
<td>C(<em>6)H(</em>{12})</td>
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<td>Amide</td>
<td>N, N-dimethyl-1,3-methyl-</td>
<td>C(<em>6)H(</em>{12})NO</td>
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<td>145</td>
<td>193</td>
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<td>Amide</td>
<td>N, N-dimethyl-1,3-oxo-Benzamide</td>
<td>C(<em>6)H(</em>{12})NO</td>
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<td>193</td>
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<tr>
<td>Alkyl Amine</td>
<td>N,N,N' N' -tetramethyl-1,4-Butanediimine</td>
<td>C(<em>6)H(</em>{12})N(_2)</td>
<td>111-51-3</td>
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<td>190</td>
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<td>Amides, Comparison Group</td>
<td>N,N-diethyl-3-methyl-Benzamide</td>
<td>C(<em>6)H(</em>{12})NO</td>
<td>134-62-3</td>
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<td>Aryl Amine</td>
<td>N,N-dimethyl-1,3-</td>
<td>C(<em>6)H(</em>{12})N(_2)</td>
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<td>191</td>
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<td>Amide</td>
<td>N,N-dimethyl-2-Propenamide</td>
<td>C(<em>6)H(</em>{12})NO</td>
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<td>C(<em>6)H(</em>{12})NO</td>
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<td>C(<em>6)H(</em>{12})N</td>
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<td>Naphthalene</td>
<td>C(_8)H(_8)</td>
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<td>Third Overtone C–H Comparison</td>
<td>n-Decane</td>
<td>C(<em>9)H(</em>{18})</td>
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<td>163, 238</td>
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<td>Amino Acid</td>
<td>N-formyl-Glycine, ethyl ester</td>
<td>C(_2)H(_4)NO(_2)</td>
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<td>Aromatic (Aryl) Compound</td>
<td>nitro-Benzene</td>
<td>C(_6)H(_5)NO(_2)</td>
<td>98-95-3</td>
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<td>Ethyl (C(_2)) Comparison Group</td>
<td>nitro-Ethane</td>
<td>C(_2)H(_5)NO(_2)</td>
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<td>nitro-Methane</td>
<td>C(_2)H(_5)NO(_2)</td>
<td>75-52-5</td>
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<td>N-methyl Formamide</td>
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<td>N-methyl Propanamide</td>
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<td>N-methyl-Acetamide</td>
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<td>192, 193, 229</td>
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<td>N-methyl-Acetamide</td>
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<td>193, 201</td>
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<td>N-methyl-Formamide</td>
<td>C(_3)H(_7)NO(_2)</td>
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<td>N-methyl-Propanamide</td>
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<td>Octadecane</td>
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<td>Octane</td>
<td>C(<em>{12})H(</em>{26})</td>
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<td>Aryl versus Alkyl Series</td>
<td>Octane</td>
<td>C(<em>{12})H(</em>{26})</td>
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<td>Pentanal</td>
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<td>Pentane</td>
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<td>X-H Compound Comparison</td>
<td>Pentane (C–C–H)</td>
<td>C(_3)H(_6)</td>
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<td>Pentanoic acid</td>
<td>C&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>Aromatic (Aryl) Compound</td>
<td>Phenanthrene</td>
<td>C&lt;sub&gt;14&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td>85-01-8</td>
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<td>Polymers and Rubbers</td>
<td>Poly(ethylene oxide) polymer</td>
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<td>Polymers and Rubbers</td>
<td>Poly(isobutyl methacrylate) polymer</td>
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<td>Polymers and Rubbers</td>
<td>Poly(vinyl butyral) polymer</td>
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<td>Polymers and Rubbers</td>
<td>Poly(vinyl chloride) polymer</td>
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<tr>
<td>Polymers and Rubbers</td>
<td>Poly(vinyl pyrrolidone) polymer</td>
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<td>Polymers and Rubbers</td>
<td>Poly(vinyl stearate) polymer</td>
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<td>Polymers and Rubbers</td>
<td>Poly(vinylidene fluoride) polymer</td>
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<td>Polymers and Rubbers</td>
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<td>Polymers and Rubbers</td>
<td>Polyethylene, chlorinated (25% Cl) polymer</td>
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<td>Polymers and Rubbers</td>
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<td>Polymers and Rubbers</td>
<td>Polystyrene polymer</td>
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<td>Carboxylic Acid</td>
<td>Propanoic acid</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>79</td>
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<td>Aromatic Compound with N or S</td>
<td>Quinoline</td>
<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;7&lt;/sub&gt;N</td>
<td>91-22-5</td>
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<td>195</td>
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<td>Heterocyclic Compound</td>
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<td>Polymers and Rubbers</td>
<td>Silicone polymer</td>
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<td>Polymers and Rubbers</td>
<td>Starch polymer</td>
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<td>Polymers and Rubbers</td>
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<tr>
<td>Third Overtone C–H Comparison</td>
<td>tert-Butanol</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;O</td>
<td>75-65-0</td>
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<td>Cyclic Ether</td>
<td>tetrahydro-2H-Pyran</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;O</td>
<td>142-68-7</td>
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<td>Cyclic Ether</td>
<td>tetrahydro-4H-Pyran-4-one</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
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<tr>
<td>Aromatic Compound with N or S</td>
<td>Thiophene</td>
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<td>Heterocyclic Compound</td>
<td>Thiophene</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;S</td>
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<td>203</td>
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<td>Third Overtone C–H Comparison</td>
<td>Toluene</td>
<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;</td>
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<td>203</td>
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<td>Third Overtone C–H Comparison</td>
<td>Trimethyl pentane</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;H&lt;sub&gt;18&lt;/sub&gt;</td>
<td>540-84-1</td>
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<tr>
<td>Alkane</td>
<td>Undecane</td>
<td>C&lt;sub&gt;11&lt;/sub&gt;H&lt;sub&gt;24&lt;/sub&gt;</td>
<td>1120-21-4</td>
<td>118, 234, 235</td>
<td>166, 236, 237</td>
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<tr>
<td>Functional Group Comparisons</td>
<td>Undecane</td>
<td>C&lt;sub&gt;11&lt;/sub&gt;H&lt;sub&gt;24&lt;/sub&gt;</td>
<td>1120-21-4</td>
<td>157</td>
<td>205</td>
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</table>

*Note: N/A indicates natural or synthetic product with no designated CAS number.*
Appendix 7: Spectra Index
by Molecular Formula
(Carbon Number)
<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Compound Name</th>
<th>Molecular formula</th>
<th>CAS Number</th>
<th>10,500 – 6300 cm⁻¹ (952 – 1587 nm)</th>
<th>7200-3800 cm⁻¹ (1389 – 2632 nm)</th>
<th>Other NIR Regions</th>
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<tbody>
<tr>
<td>Carboxylic Acid</td>
<td>Formic acid</td>
<td>CH₂O₂</td>
<td>64-18-6</td>
<td>154, 230</td>
<td>202, 231</td>
<td>—</td>
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<tr>
<td>Amide</td>
<td>Formamide</td>
<td>CH₄NO</td>
<td>75-12-7</td>
<td>144, 228</td>
<td>192, 229</td>
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<tr>
<td>Methyl Comparison Group</td>
<td>nitro-Methane</td>
<td>CH₂NO₂</td>
<td>75-52-5</td>
<td>135</td>
<td>183</td>
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<tr>
<td>Methyl Comparison Group</td>
<td>dichloromethyl Silane</td>
<td>CH₂Cl₂</td>
<td>75-54-7</td>
<td>135</td>
<td>183</td>
<td>—</td>
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<tr>
<td>Alkyl (mono-OH)</td>
<td>Methanol</td>
<td>CH₄O</td>
<td>67-56-1</td>
<td>119, 208, 209</td>
<td>167, 210</td>
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<td>Methyl Comparison Group</td>
<td>Methanol</td>
<td>CH₄O</td>
<td>67-56-1</td>
<td>135</td>
<td>183</td>
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<td>Ethyl (C₂) Comparison Group</td>
<td>1,2-dibromo-Ethane</td>
<td>C₂H₅Br₂</td>
<td>106-93-4</td>
<td>133</td>
<td>181</td>
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<tr>
<td>Ethyl (C₂) Comparison Group</td>
<td>1,1,1-trichloro-Ethane</td>
<td>C₂H₅Cl₃</td>
<td>71-55-6</td>
<td>133</td>
<td>181</td>
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<tr>
<td>Ethyl (C₂) Comparison Group</td>
<td>1,2-dichloro-Ethane</td>
<td>C₂H₅Cl₂</td>
<td>107-06-2</td>
<td>133</td>
<td>181</td>
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<tr>
<td>Methyl Comparison Group</td>
<td>Formic acid, methyl ester</td>
<td>C₂H₅O₂</td>
<td>107-31-3</td>
<td>135</td>
<td>183</td>
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<td>Ethyl (C₂) Comparison Group</td>
<td>2-bromo-Ethanol</td>
<td>C₂H₅BrO</td>
<td>540-51-2</td>
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<td>181</td>
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<td>Amide</td>
<td>N-methyl Formamide</td>
<td>C₂H₅NO</td>
<td>123-39-7</td>
<td>145</td>
<td>193</td>
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<td>Ethyl (C₂) Comparison Group</td>
<td>nitro-Ethane</td>
<td>C₂H₅NO₂</td>
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<td>181</td>
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<td>1,2-Ethanediol</td>
<td>C₂H₅O₂</td>
<td>107-21-1</td>
<td>120</td>
<td>168</td>
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<td>Alkyl Amine</td>
<td>1,2-Propanediamine</td>
<td>C₂H₅N₂</td>
<td>78-90-0</td>
<td>142, 224</td>
<td>190, 225</td>
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<td>Alkylhyde</td>
<td>2-Propynal</td>
<td>C₂H₅O</td>
<td>624-67-9</td>
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<td>Alkyne</td>
<td>3-chloro-1-Propyne</td>
<td>C₂H₅Cl</td>
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<td>Ketone</td>
<td>2-Propanone (Acetone)</td>
<td>C₂H₅O</td>
<td>67-64-1</td>
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<td>2-Propanol-1-ol</td>
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<td>Acetone</td>
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<td>163, 238</td>
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<td>Propanoic acid</td>
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<td>Propyl Comparison Group</td>
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<td>C₃H₇Cl</td>
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<td>Propyl Comparison Group</td>
<td>2-chloro Propane</td>
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<td>75-29-6</td>
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<td>Amides, Comparison Group</td>
<td>N-methyl-Acetamide</td>
<td>C₃H₇NO</td>
<td>79-16-3</td>
<td>153</td>
<td>193, 201</td>
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<td>Acid vs. Amide vs. Ester Comparison</td>
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<td>C₂H₆O</td>
<td>71-23-8</td>
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<td>C₂H₆O</td>
<td>71-23-8</td>
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<td>184</td>
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<td>Alkyl (mono-OH)</td>
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<td>Propyl Comparison Group</td>
<td>2-Propanol</td>
<td>C₂H₆O</td>
<td>67-63-0</td>
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<td>184</td>
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<td>1,2-Propanediol</td>
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<td>X-H Compound Comparison</td>
<td>2-Propanamide (C–NH)</td>
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<td>Molecular Formula</td>
<td>Spectra&lt;sup&gt;2&lt;/sup&gt;</td>
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<td>Amide</td>
<td>N-methyl-Acetamide</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;N=O</td>
<td>79-16-3</td>
<td>144, 145, 228</td>
<td>192, 193, 229</td>
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<td>Alcohol (mono-OH)</td>
<td>1-Butanol</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;O</td>
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<td>167, 210</td>
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<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;O</td>
<td>71-36-3</td>
<td>131</td>
<td>179</td>
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<tr>
<td>Alcohol (mono-OH)</td>
<td>2-Butanol</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;O</td>
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<td>Four-Carbon (Butyl) Comparison</td>
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<td>Butyl Comparison Group</td>
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<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;O</td>
<td>78-92-2</td>
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<td>X-H Compound Comparison</td>
<td>2-Butanol (C-OH)</td>
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<td>Alcohol (mono-OH)</td>
<td>2-methyl-2-Propanol</td>
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<td>118, 119, 209, 234, 235</td>
<td>166, 167, 236, 237</td>
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<td>2-methyl-2-Propanol</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;O</td>
<td>75-65-0</td>
<td>157, 234, 235</td>
<td>205, 236, 237</td>
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<tr>
<td>Third Overtone C–H Comparison</td>
<td>tert-Butanol</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;O</td>
<td>75-65-0</td>
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<td>514-15-6</td>
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<td>Butanediol Series</td>
<td>1,2-Butanediol</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>584-03-2</td>
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<td>169, 211</td>
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<td>1,3-Butanediol</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>169, 211</td>
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<td>Butanediol Series</td>
<td>1,4-Butanediol</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>110-63-4</td>
<td>121</td>
<td>169, 211</td>
<td></td>
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<tr>
<td>Alcohol (diol)</td>
<td>2,3-Butanediol</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>Polyene</td>
<td>1,3-Cyclohexadiene</td>
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<td>Ketone</td>
<td>2-Cyclohexen-1-one</td>
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<td>Heterocyclic (5-member ring)</td>
<td>4,5-dihydro-2-(2-propenythio)-Thiazole</td>
<td>C₆H₉NS₂</td>
<td>3571-74-2</td>
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<td>1-Heptyne</td>
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<td>Cycloheptene</td>
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<td>Alkane &amp; Cycloalkane Comparison</td>
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<td>125, 216</td>
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<td>142-82-5</td>
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<td>182</td>
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<td>1,7-Heptanediamine</td>
<td>C₇H₁₂N₂</td>
<td>646-19-5</td>
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<td>2-bromo-Benzaldehyde</td>
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<td>2-chloro-Benzaldehyde</td>
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<td>C₇H₆O</td>
<td>100-52-7</td>
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<td>197</td>
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<td>methyl-Benzene</td>
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<td>166, 197, 236, 237</td>
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<td>166, 199</td>
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<td>Third Overtone C–H Comparison</td>
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<td>3-methyl-Phenol</td>
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<td>4-methyl-Phenol</td>
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<td>methoxy-Benzene</td>
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<td>Source</td>
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<td>C₈H₈N</td>
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<td>Aromatic (Aryl) Compound 1,4-dimethyl-Benzene (xylene)</td>
<td>C₈H₁₀O</td>
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<td>Aromatic (Aryl) Compound 3-ethyl-Pyridine</td>
<td>C₇H₉N</td>
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<td>1,3-Cyclooctadiene</td>
<td>Ether 2-phenox-Ethanol</td>
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<td>N,N-dimethyl-1,3-Benzenediamine</td>
<td>Aryl Amine 1,7-Octadiene</td>
<td>C₈H₁₂N₂</td>
<td>2836-04-2</td>
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<td>Polyene 1,7-Octadiene</td>
<td>C₉H₁₄</td>
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<td>Alkyne 1-Octyne</td>
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<td>188, 227</td>
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<td>4-Octyne</td>
<td>Alkyne 4-Octyne</td>
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<td>1942-45-6</td>
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<td>N,N-dimethyl-3-oxo-Butanamide</td>
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<td>Isomerism Comparison Group 2,2,4-trimethylpentane</td>
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<td>166, 196, 220, 221, 236, 237</td>
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<td>2,4-dimethyl-Benzaldehyde</td>
<td>Aldehyde, Substituted Aromatic 2,4-dimethyl-Benzaldehyde</td>
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<td>Carboxylic Acid 1H-Indole</td>
<td>C₉H₈NO₂</td>
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<td>Alky Amine N,N,N',N'-tetramethyl-1,4-Butanediamine</td>
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<td>111-51-3</td>
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<td>Aryl Amine 1H-Indole</td>
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<td>Aromatic Compound with N or S Indole, 1-H</td>
<td>C₉H₈N</td>
<td>120-72-9</td>
<td>143</td>
<td>191</td>
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<td>Amide 2,4-dimethyl-Benzaldehyde</td>
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<td>Benzenepropanal</td>
<td>Polyfunctional Comparison Benzenepropanal</td>
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<td>Quinoline</td>
<td>Aromatic Compound with N or S Quinoline</td>
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<td>Heterocyclic Compound 1H-Indole</td>
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<td>Compound Name</td>
<td>Molecular formula</td>
<td>CAS Number</td>
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<td>7200-3800 cm⁻¹ (1389 – 2632 nm)</td>
<td>Other NIR Regions</td>
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<td>2,4,6-trimethyl-Benzaldehyde</td>
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<td>193</td>
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<td>Decanal</td>
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<td>Decanoic acid</td>
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<td>D-Valine, 3-methyl, 1,1-dimethylethyl ester</td>
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<td>C₁₀H₂₂</td>
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<td>1-Decanamine</td>
<td>C₁₀H₂₃N</td>
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<td>Undecane</td>
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<td>Polymers and Rubbers</td>
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*Note: N/A indicates natural or synthetic product with no designated CAS number*
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Practical Guide to Interpreive Near-Infrared Spectroscopy

Containing focused, comprehensive coverage, Practical Guide to Interpreive Near-Infrared Spectroscopy gives you the tools necessary to interpret NIR spectra. The authors present extensive tables, charts, and figures with NIR absorption band assignments and structural information for a broad range of functional groups, organic compounds, and polymers. They include visual spectral representation of all major compound functional groupings and NIR frequency ranges. Organized by functional group type and chemical structure, based on standard compound classification, the chapters are easy to follow and understand. The use of Molecular Formula and CAS Number indexing prevents the confusion that can occur when using only common chemical names to identify compounds.

Features

- Offers more than 500 figures representing all the major functional groups and their NIR frequency ranges
- Contains over 120 pages of tables and charts illustrating overlapping spectra
- Covers NIR spectra for organic compounds including alkanes, carboxylic acids, amines, aldehydes, heterocyclic compounds, amino acids, and aldehydes
- Provides comprehensive appendices with spectra-structure correlations, example spectra, and other useful data for interpreting NIR spectra

Interpretive spectroscopy provides a basis for the establishment of cause-and-effect relationships between spectrometer response and the chemical properties of the samples. While many books available on NIR cover a range of applications and topics from a broad perspective, most of them barely touch on structure correlation and interpretation of spectra. The first and arguably the only book to tackle this intriguing and challenging area, Practical Guide to Interpreive Near-Infrared Spectroscopy presents the most detailed discussion of the subject to date.