Interpretation of Infrared Spectra, A Practical Approach

John Coates

Interpretation of Infrared Spectra, A Practical Approach

John Coates
Coates Consulting, Newtown, USA

The vibrational spectrum of a molecule is considered to be a unique physical property and is characteristic of the molecule. As such, the infrared spectrum can be used as a fingerprint for identification by the comparison of the spectrum from an "unknown" with previously recorded reference spectra. This is the basis of computer-based spectral searching. In the absence of a suitable reference database, it is possible to effect a basic interpretation of the spectrum from first principles, leading to characterization, and possibly even identification of an unknown sample. This first principles approach is based on the fact that structural features of the molecule, whether they are the backbone of the molecule or the functional groups attached to the molecule, produce characteristic and reproducible absorptions in the spectrum. This information can indicate whether there is backbone to the structure and, if so, whether the backbone consists of linear or branched chains. Next it is possible to determine if there is unsaturation and/or aromatic rings in the structure. Finally, it is possible to deduce whether specific functional groups are present. If detected, one is also able to determine local orientation of the group and its local environment and/or location in the structure. The origins of the sample, its prehistory, and the manner in which the sample is handled all have impact on the final result. Basic rules of interpretation exist and, if followed, a simple, first-pass interpretation leading to material characterization is possible. This article addresses these issues in a simple, logical fashion. Practical examples are included to help guide the reader through the basic concepts of infrared spectral interpretation.

1 INTRODUCTION

The qualitative aspects of infrared spectroscopy are one of the most powerful attributes of this diverse and versatile analytical technique. Over the years, much has been published in terms of the fundamental absorption frequencies (also known as group frequencies) which are the key to unlocking the structure–spectral relationships of the associated molecular vibrations. Applying this knowledge at the practical routine level tends to be a mixture of art and science. While many purists will argue against this statement, this author believes that it is not possible to teach a person to become proficient as an interpretive spectroscopist by merely presenting the known relationships between structure and the observed spectra. Instead, the practical approach, which has been adopted in this text, is to help the reader appreciate the visual aspects of the spectroscopy and how to interpret these relative to the structure and chemistry of the sample. This is achieved by recognizing characteristic shapes and patterns within the spectrum, and by applying the information obtained from published group frequency data, along with other chemical and physical data from the sample.

Included in the text is a discussion of the interrelationships that exist between the practical side of acquiring the spectrum, the chemistry and physics of the sample under study, the physical interactions of the sample with its environment, and the impact of the structure on the spectrum. In essence, the interpretation of infrared spectra is much more than simply assigning group frequencies. The spectrum is rich in information, and this article is intended to help the reader to extract the maximum using the knowledge available for the sample and the acquired spectral data. One important factor to bear in

mind is that a successful interpretation is based not only on the *presence* of particular bands within the spectrum, but also the *absence* of other important bands. Complete classes of compounds can be rapidly excluded during the interpretation by the use of *no-band* information.

It must be understood that this article addresses the issue of infrared spectral interpretation from the perspective of the average operator of an infrared instrument. It is not a detailed treatise on the theory of infrared spectroscopy where the modes of vibration are discussed in terms of group theory, and where mathematical models are used to compare theoretical and observed values for the fundamental vibrations of a molecule. There are many excellent texts that cover this subject.[1-4] Instead, this article focuses on the day-to-day problems associated with characterizing a material or attempting to perform some form of identification. One of the main challenges in presenting a text on spectral interpretation is to form a balance between the theory that is needed to appreciate the links between molecular structure and the observed spectrum and the practice. For this reason, a minimum amount of relevant theory is included in the next section, which provides a basic understanding of why the spectrum exists, how it is formed, and what factors contribute to the complexity of observed spectra. It has been assumed that the reader has a fundamental knowledge of molecular theory and bonding, and that there is an understanding of basic structures, in particular for organic compounds.

Infrared spectral interpretation may be applied to both organic and inorganic compounds, and there are many specialized texts dealing with these compounds, in combination and as individual specialized texts. There are too many to reference comprehensively, and the reader is directed to a publication that provides a bibliography of the most important reference texts.[5] However, the most informative general reference texts are included,[6-14] with books by Socrates[10] and Lin-Vien[11] being recommended for general organics, and by Nakamoto[13] and Nyquist et al.[14] for inorganics (salts and coordination compounds). There are numerous specialized texts dealing with specific classes of materials, and undoubtedly polymers and plastics form the largest individual class.[15-17] In this particular case, texts by Hummel and Scholl[16] and Koenig[17] provide a good basic understanding.

The following comments are made relative to the conventions used within this article. The term frequency is used for band/peak position throughout, and this is expressed in the commonly used units of wavenumber (cm^{-1}). The average modern infrared instrument records spectra from an upper limit of around $4000\,cm^{-1}$ (by convention) down to $400\,cm^{-1}$ as defined by the optics of the instrument (commonly based on potassium

bromide, KBr). For this reason, when a spectral region is quoted in the text, the higher value will be quoted first, consistent with the normal left-to-right (high to low cm^{-1}) representation of spectra. Also, the terms infrared band, peak and absorption will be used interchangeably within the text to refer to a characteristic spectral feature.

The spectral group frequencies provided in this text were obtained from various literature sources published over the past 30 years, and most of these are included in the cited literature. Every attempt to ensure accuracy has been taken; however, there will be instances when individual functional groups may fall outside the quoted ranges. This is to be expected for several reasons: the influences of other functional groups within a molecule, the impact of preferred spatial orientations, and environmental effects (chemical and physical interactions) on the molecule.

The preferred format for presenting spectral data for qualitative analysis is in the percentage transmittance format, which has a logarithmic relationship $(-\log_{10})$ with respect to the linear concentration format (absorbance). This format, which is the natural output of most instruments (after background ratio), provides the best dynamic range for both weak and intense bands. In this case, the peak maximum is actually represented as a minimum, and is the point of lowest transmittance for a particular band.

2 THE ORIGINS OF THE INFRARED SPECTRUM

In the most basic terms, the infrared spectrum is formed as a consequence of the absorption of electromagnetic radiation at frequencies that correlate to the vibration of specific sets of chemical bonds from within a molecule. First, it is important to reflect on the distribution of energy possessed by a molecule at any given moment, defined as the sum of the contributing energy terms (Equation 1):

$$E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} + E_{\text{translational}}$$

$$(1)$$

The translational energy relates to the displacement of molecules in space as a function of the normal thermal motions of matter. Rotational energy, which gives rise to its own form of spectroscopy, is observed as the tumbling motion of a molecule, which is the result of the absorption of energy within the microwave region. The vibrational energy component is a higher energy term and corresponds to the absorption of energy by a molecule as the component atoms vibrate about the mean center of their chemical bonds. The electronic component is linked to the energy transitions of electrons as they

are distributed throughout the molecule, either localized within specific bonds, or delocalized over structures, such as an aromatic ring. In order to observe such electronic transitions, it is necessary to apply energy in the form of visible and ultraviolet radiation (Equation 2):

$$E = hv \qquad \text{frequency/energy} \qquad (2)$$

The fundamental requirement for infrared activity, leading to absorption of infrared radiation, is that there must be a net change in dipole moment during the vibration for the molecule or the functional group under study. Another important form of vibrational spectroscopy is Raman spectroscopy, which is complementary to infrared spectroscopy. The selection rules for Raman spectroscopy are different to those for infrared spectroscopy, and in this case a net change in bond polarizability must be observed for a transition to be Raman active. The remaining theoretical discussion in this article will be limited to a very simple model for the infrared spectrum. The reader is encouraged to refer to more complete texts[2–4] for detailed discussion of the fundamentals.

While it was stated that the fundamental infrared absorption frequencies are not the only component to be evaluated in a spectral interpretation, they are the essence and foundation of the art. For the most part, the basic model of the simple harmonic oscillator and its modification to account for anharmonicity suffice to explain the origin of many of the characteristic frequencies that can be assigned to particular combinations of atoms within a molecule. From a simple statement of Hooke's law we can express the fundamental vibrational frequency of a molecular ensemble according to Equation (3):

$$v = \frac{1}{2\pi c} \sqrt{\frac{\kappa}{\mu}} \qquad (3)$$

where v = fundamental vibration frequency, κ = force constant, and μ = reduced mass. The reduced mass, $\mu = m_1 m_2/(m_1 + m_2)$, where m_1 and m_2 are the component masses for the chemical bond under consideration.

This simple equation provides a link between the strength (or springiness) of the covalent bond between two atoms (or molecular fragments), the mass of the interacting atoms (molecular fragments) and the frequency of vibration. Although simple in concept, there is a reasonably good fit between the bond stretching vibrations predicted and the values observed for the fundamentals.

This simple model does not account for repulsion and attraction of the electron cloud at the extremes of the vibration, and does not accommodate the concept of bond dissociation at high levels of absorbed energy. A model incorporating anharmonicity terms is commonly used to interpret the deviations from ideality and the overall energy–spatial relationship during the vibration

of a bond between two atomic centers. The fundamental, which involves an energy transition between the ground state and the first vibrational quantum level, is essentially unaffected by the anharmonicity terms. However, transitions that extend beyond the first quantum level (to the second, third, fourth, etc.), which give rise to weaker absorptions, known as overtones, are influenced by anharmonicity, which must be taken into account when assessing the frequency of these higher frequency vibrations.

Having defined the basis for the simple vibration of an atomic bond, it is necessary to look at the molecule as a whole. It is very easy to imagine that there is an infinite number of vibrations, which in reality would lead to a totally disorganized model for interpretation. Instead, we describe the model in terms of a minimum set of fundamental vibrations, based on a threefold set of coordinate axes, which are known as the normal modes of vibration. All the possible variants of the vibrational motions of the molecule can be reduced to this minimum set by projection on to the threefold axes. It can be shown that the number of normal modes of vibration for a given molecule can be determined from Equations (4) and (5):

$$\text{number of normal modes} = 3N - 6 \text{ (nonlinear)} \quad (4)$$
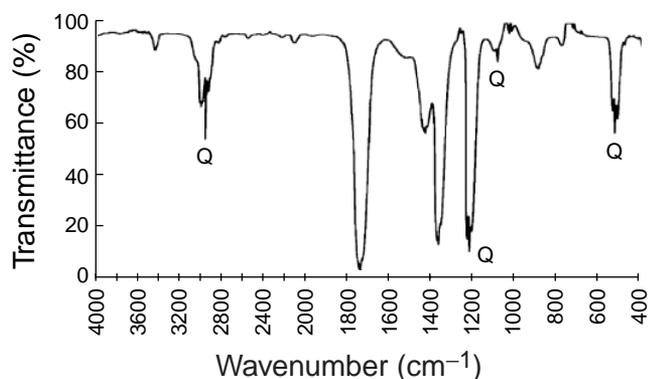
$$= 3N - 5 \text{ (linear)} \qquad (5)$$

where N is the number of component atoms in the molecule.

In practice, apart from the simplest of compounds, most molecules have nonlinear structures, except where a specific functional group or groups generate a predominant linear arrangement to the component atoms. If we calculate the number of modes for a simple hydrocarbon, such as methane (nonlinear, tetrahedral structure), a value of nine is obtained. This would imply that nine sets of absorption frequencies would be observed in the spectrum of methane gas. In reality, the number observed is far less, corresponding to the asymmetric and symmetric stretching and bending of the C−H bonds about the central carbon atom. The reason for the smaller than expected number is that several of the vibrations are redundant or degenerate, that is, the same amount of energy is required for these vibrations. Note that although a small number of vibrational modes is predicted, and in fact observed, the appearance of the methane spectrum at first glance is far more complex than expected, especially at higher spectral resolutions ($<1 \, \text{cm}^{-1}$). At relatively high resolutions, a fine structure is superimposed, originating from rotational bands, which involve significantly lower energy transitions. Each of the sets of vibrational–rotational absorptions manifest this superimposed fine structure for low-molecular-weight gaseous compounds, methane being a good example. Several medium-molecular-weight
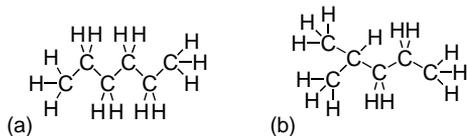
compounds may also show evidence of some fine structure when studied in the vapor state. For example, it is common to observe the sharp feature (or spike) assigned to the Q-branch of the vibrational–rotational spectrum, as indicated by the vapor spectrum of acetone (Figure 1).

If we proceed up the homologous series from methane (CH_4) to *n*-hexane (C_6H_{14}), there are 20 component atoms, which would imply 54 normal modes. In this case the picture is slightly more complex. Methane is a unique molecule, and only contains one type of C−H group – no other types of bond exist in this molecule. In hexane there are several types of bond and functionality. For reference, a simple two-dimensional representation of the structure is provided in Figure 2(a).

As we can see, there are two terminal methyl groups (CH_3) and four connecting methylene groups (CH_2). Each of these groups has its corresponding C−H stretching and bending vibrations (see later text for the actual absorption frequencies). Also, the methyl groups are linked to a neighboring methylene group, which is in turn linked to neighboring methylene groups, and so on. These linkages feature carbon–carbon bonds. For interpretation, we view the C−H groups as functional groups, giving rise to the common group frequencies, and the C−C linkages as the backbone, producing the skeletal vibrations. As a rule, a group frequency may be applied generally to most compounds featuring the corresponding functional group. In contrast, the skeletal vibrations are unique to a specific molecule. The group frequencies help to characterize a compound, and the
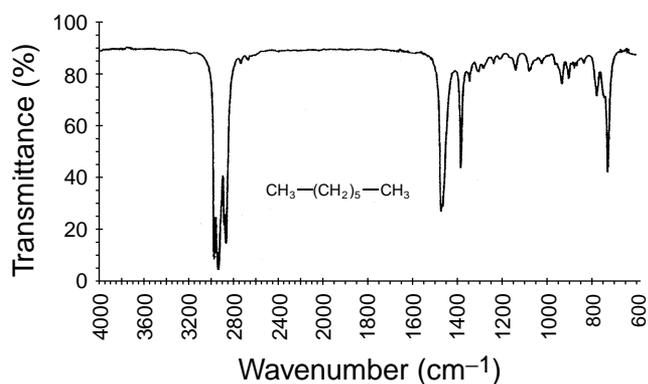
combination of the bands associated with these group frequencies and the skeletal frequencies are used to identify a specific compound. The latter forms the basis of the use of reference spectra for spectral matching by visual comparison or by computer-based searching, for the identification of an unknown from its infrared spectrum.

The group frequencies may be viewed quantitatively, as well as qualitatively. A given absorption band assigned to a functional group increases proportionately with the number times that functional group occurs within the molecule. For example, in the spectrum of *n*-hexane, the intensities measured for the group frequency absorptions assigned to methyl and methylene correspond to four methylene groups and two methyl groups on a relative basis, when compared with other hydrocarbon compounds within a homologous series. For example, if we examine the C−H stretching (or bending) band intensities for CH_3 and CH_2, we will observe that the relative intensities of CH_3 to CH_2 decrease with increase in chain length. Restated, there is less methyl contribution and more methylene contribution with increase in chain length/molecular weight. The reverse holds true if we examine the spectra of linear hydrocarbons with chain lengths shorter than that of hexane.
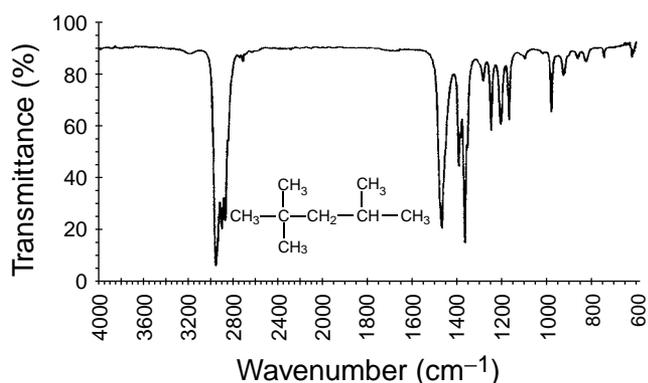
If we apply these ideas to a different hexane isomer, such as isohexane (2-methylpentane), we would see significant differences in the spectrum. These can be explained by evaluating the structure (Figure 2b), which contains three methyl groups, two methylene groups, and a group that contains a single hydrogen attached to carbon (the methyne group). This adds a new complexity to the spectrum: the main absorptions show differences in appearance, caused by the changes in relative band intensities, splittings of absorptions occur (originating from spatial/mechanical interaction of adjacent methyl groups), and changes are observed in the distributions of the C−C skeletal vibrations, in part due to the splitting by the methyl side chain. Further discussions concerning the impact of chain branching are covered later in this article. Comparison of Figures 3 and 4 provides a graphical representation of the aspects discussed for the hexanes of structurally similar compounds, i.e. *n*-heptane and isooctane.

From a first-order perspective, the idea of the quantitative aspects of the group frequencies carries through for most functional groups, and the overall spectrum is essentially a composite of the group frequencies, with band intensities in part related to the contribution of each functional group in the molecule. This assumes that the functional group does give rise to infrared absorption frequencies (most do), and it is understood that each group has its own unique contribution based on its extinction coefficient (or infrared absorption cross-section).

Returning to the fundamental model, we should now look at the larger picture. In reality, we assign the

Figure 1 Vapor spectrum of acetone with characteristic Q-branch slitting, denoted by Q. Copyright Coates Consulting.

Figure 2 Structures for hexane isomers: (a) *n*-hexane and (b) isohexane (2-methylpentane). Copyright Coates Consulting.

Figure 3 Attenuated total reflectance (ATR) spectrum of *n*-heptane. Copyright Coates Consulting.

Figure 4 ATR spectrum of 2,2,4-trimethylpentane (isooctane). Copyright Coates Consulting.

observed absorption frequencies in the infrared spectrum to much more that just simple harmonic (or anharmonic) stretching vibrations. In practice, we find that various other deformation motions (angular changes), such as bending and twisting about certain centers within a molecule, also have impact, and contribute to the overall absorption spectrum. By rationalizing the effort needed to move the atoms relative to each other, one can appreciate that it takes less energy to bend a bond than to stretch it. Consequently, we can readily accept the notion that the stretching absorptions of a vibrating chemical bond occur at higher frequencies (wavenumbers) than the corresponding bending or bond deformation vibrations, with the understanding, of course, that energy and frequency are proportionally related. A good example is the C−H set of vibrations, observed in the hydrocarbon spectra, and in virtually all organic compounds. Here, the simple C−H stretching vibrations for saturated aliphatic species occur between 3000 and 2800 cm^{-1}, and the corresponding simple bending vibrations nominally occur between 1500 and 1300 cm^{-1}.

Next in our understanding is that it can take slightly more energy to excite a molecule to an asymmetric than a symmetric vibration. While this might be less intuitive, it is still a rational concept, and therefore easy to understand and accept. Again, we see a good example with the C−H stretch of an aliphatic compound (or fragment), where we observe the asymmetric C−H stretch of the methyl and methylene groups (2960 and 2930 cm^{-1}, respectively) occurring at slightly higher frequency than symmetric vibrations (2875 and 2855 cm^{-1}, respectively for methyl and methylene). For the most part, this simple rule holds true for most common sets of vibrations. Naturally there are always exceptions, and a breakdown of the rationale may occur when other effects come into play, such as induced electronic, spatial or entropy-related effects.

There are many other spatially related scenarios that tend to follow well-orchestrated patterns, examples being in-plane and out-of-plane vibrations, the differences between *cis* and *trans* spatial relationships, and a variety of multicentered vibrations that are defined as twisting or rocking modes. Many of these are exhibited with the C−H vibrations that occur in saturated, unsaturated and aromatic compounds. Molecular symmetry of the static or the dynamic (during vibration) molecule has a large impact on the spectrum, in addition to factors such as relative electronegativity, bond order and relative mass of the participating atoms.

Finally, while discussing the vibrational origins of infrared spectra, it is worth commenting that further complexity may be noted in the spectrum, beyond what is expected based on the fundamentals. As noted, transitions to higher energy levels, although theoretically not allowed, can occur and these give rise to overtone bands, which in the mid-infrared region occur at approximately twice the fundamental frequency for the first overtone. Higher overtones exist, typically the second (3 × fundamental) and third (4 × fundamental), and sometimes higher, and these are observed, with extremely low intensity, relative to the fundamental in the near-infrared spectral regions, between 800 and 2500 nm (12 500 and 4000 cm^{-1}). Other types of bands that can add complexity to a spectrum are combination bands (sum and difference), bands due to transitions from energy states higher than the ground state or "hot bands", and bands due to interactions between a weaker overtone or combination band and a fundamental of the same or similar frequency, known as Fermi resonance bands. In the latter case, two relatively strong absorptions are observed, where normally only a single absorption is expected for the fundamental.[3]

As additional functional groups are added to a basic backbone structure, forming a more complex molecule, additional bands are observed, either directly associated with the fundamental vibrations of the functional groups, or indirectly related to interactions between component

functional groups or the basic substructure. Such interactions can be severe, and result in overwhelming distortions in the appearance of the spectrum, a good example being hydrogen bonding. This will be dealt with in depth later.

3 SPECTRAL INTERPRETATION BY APPLICATION OF VIBRATIONAL GROUP FREQUENCIES

This section includes tabulated data relative to the most significant group frequencies for the most common functional groups and structural components found in organic compounds. Brief reference is also made to simple inorganic compounds, in the form of simple ionic species. More detailed listings can be found in published literature, and the reader is encouraged to acquire one or more of these reference texts.[9–13] As already indicated, the use of tabulated data is only a part of the interpretation process, and other facets of the spectrum must be taken into account.

To help gain an understanding of infrared spectral interpretation, it is instructive to start at the root of most organic compounds, namely the fundamental backbone or the parent hydrocarbon structure. We shall start with the simple, aliphatic hydrocarbon, which is at the root of most aliphatic compounds. Aliphatic hydrocarbons exist in simple linear chains, branched chains and in cyclic structures – examples of the linear and branched chain scenarios were provided earlier for hexane isomers. Any one molecule may exist with one or more of these component structures. The infrared spectrum can provide information on the existence of most of these structures, either directly or by inference.

The introduction of unsaturation in the form of a double or triple bond has a profound impact on the chemistry of the molecule, and likewise it has a significant influence on the infrared spectrum. Similarly, the same is observed when an aromatic structure is present within a molecule. Infrared spectroscopy is a powerful tool for identifying the presence of these functionalities. It provides information specific to the group itself, and also on the interaction of the group with other parts of the molecule and on the spatial properties of the group. Examples of these include conjugation between a double bond and another unsaturated center, an aromatic ring or a group, such as a carbonyl (C=O), and the orientation or location of the double bond within the molecule, such as *cis* or *trans* and medial or terminal. It should be noted that *cis/trans* relationships are not specific to unsaturated hydrocarbons, and the terminology is referenced elsewhere, such as with secondary amide structures. Again, the associated changes in the spatial arrangement of the groups involved is reflected in the infrared spectrum as additional bands and added complexity.

As we move on to simple organic compounds, where one or more functional groups or heteroatoms are added to the molecule, we see many changes occurring in the spectrum. These result from the bonding associated with the functional group, and also local disturbances to the basic backbone spectrum that relate again to spatial changes and also to local and neighboring electronic effects. Examples of such functionalities are halogens, simple oxygen species, such as hydroxy and ether groups, and amino compounds. Carbonyl compounds, where the added functional group includes the C=O bond, also provide very profound contributions to the spectrum, and because of the wide diversity of these compounds they are best dealt with as a separate class.

A very characteristic group of compounds, from a spectral point of view, are the multiple-bonded nitrogen compounds, such as cyanides and cyanates. These typically have very characteristic absorptions, which are easy to assign, and are free from spectral interferences. The same can be said for some of the hydrides of heteroatoms, such as sulfides (thiols), silanes, and phosphines. Finally, there are other, oxygen-containing functional groups, as encountered in the nitrogen-oxy (NO_x), phosphorus-oxy (PO_x), silicon-oxy (SiO_x), and sulfur-oxy (SO_x) compounds. These are sometimes more difficult to identify from first principles, and a knowledge of the presence of the heteroatom is helpful. The spectra are characteristic, but many of the oxy absorptions occur within a crowded and highly overlapped region of the spectrum, mainly between 1350 and 950 cm^{-1}. Also, many of these compounds feature C−O bonding, which is common in other frequently encountered functionalities such as ethers and esters.

3.1 The Hydrocarbon Species and Molecular Backbone

In this section we include the characteristic absorption frequencies encountered for the parent hydrocarbon species and the associated backbone or substituent group. This includes aliphatic and aromatic structures. The spectral contributions are characterized, as previously noted, as C−H stretching and bending vibrations and C−C vibrations (stretching and bending), which for the most part are unique for each molecule, and are generally described as skeletal vibrations. In the case of aromatic compounds, ring C=C−C stretching and bending vibrations are highly characteristic, and are diagnostic. Likewise, the same can be said for the unsaturated carbon−carbon multiple bonding in alkene and alkyne structures.

Table 1 Saturated aliphatic (alkane/alkyl) group frequencies

Group frequency (cm^{-1})	Functional group/assignment
	Methyl ($-$CH$_3$)
2970–2950/2880–2860	Methyl C$-$H asym./sym. stretch
1470–1430/1380–1370	Methyl C$-$H asym./sym. bend
1385–1380/1370–1365	*gem*-Dimethyl or "iso"- (doublet)
1395–1385/1365	Trimethyl or "*tert*-butyl" (multiplet)
	Methylene ($>$CH$_2$)
2935–2915/2865–2845	Methylene C$-$H asym./sym. stretch
1485–1445	Methylene C$-$H bend
750–720	Methylene $-$(CH$_2$)$_n-$ rocking ($n \geq 3$)
1055–1000/1005–925	Cyclohexane ring vibrations
	Methyne ($>$CH$-$)
2900–2880	Methyne C$-$H stretch
1350–1330	Methyne C$-$H bend
1300–700	Skeletal C$-$C vibrations
	Special methyl ($-$CH$_3$) frequencies
2850–2815	Methoxy, methyl ether O$-$CH$_3$, C$-$H stretch
2820–2780	Methylamino, N$-$CH$_3$, C$-$H stretch

Table 2 Olefinic (alkene) group frequencies

Origin	Group frequency, wavenumber (cm^{-1})	Assignment
C=C	1680–1620	Alkenyl C=C stretch
	1625	Aryl-substituted C=C
	1600	Conjugated C=C
C$-$H	3095–3075 +3040–3010	Terminal (vinyl) C$-$H stretch
	3095–3075	Pendant (vinylidene) C$-$H stretch
	3040–3010	Medial, *cis*- or *trans*-C$-$H stretch
C$-$H	1420–1410	Vinyl C$-$H in-plane bend
	1310–1290	Vinylidene C$-$H in-plane bend
C$-$H	995–985 + 915–890	Vinyl C$-$H out-of-plane bend
	895–885	Vinylidene C$-$H out-of-plane bend
C$-$H	970–960	*trans*-C$-$H out-of-plane bend
	700 (broad)	*cis*-C$-$H out-of-plane bend

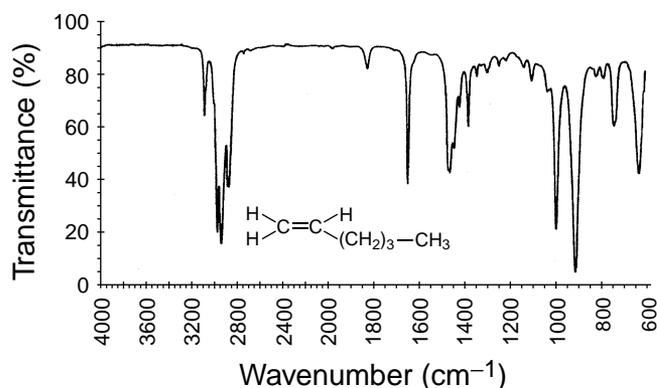### 3.1.1 Saturated Aliphatic and Alicyclic Compounds

See Table 1. The C$-$H stretch vibrations for methyl and methylene are the most characteristic in terms of recognizing the compound as an organic compound containing at least one aliphatic fragment or center. The bending vibrations help to tell more about the basic structure. For example, a strong methylene/methyl band (1470 cm^{-1}) and a weak methyl band (1380 cm^{-1}), plus a band at 725–720 cm^{-1} (methylene rocking vibration) is indicative of a long-chain linear aliphatic structure (note that splitting may be observed for the 1470 and 720 cm^{-1} bands, which is indicative of a long-chain compound, and is attributed to a crystallinity and a high degree of regularity for the linear backbone structure). In contrast, strong methyl bands, showing significant splitting, and a comparatively weaker methylene/methyl band indicate chain branching, and the possibility of isopropyl or *tert*-butyl substituents (depending on the amount of splitting, and the relative band intensities). A comparison between linear and branched chain hydrocarbons can be seen in Figures 3 and 4, where in the case of isooctane, both isopropyl and *tert*-butyl groups are present.

3.1.2 Unsaturated Compounds

See Table 2. As already commented upon, the saturated hydrocarbon C$-$H stretching absorptions all occur below 3000 cm^{-1}. Any band structures observed between 3150 and 3000 cm^{-1} are almost exclusively indicative of unsaturation (C=C$-$H) and/or aromatic rings. The

Figure 5 ATR spectrum of 1-hexene. Copyright Coates Consulting.

unsaturated hydrocarbons featuring C=C, with attached hydrogens, usually occur as either a single or a pair of absorptions, in the ranges indicated in Table 2. As noted, the number of bands and their positions are indicative of the double bond location and the spatial arrangement around the double bond. The position of the C=C stretching frequency does vary slightly as a function of orientation around the double bond, but it is less informative than the C$-$H information. The C$-$H out-of-plane bending is typically the most informative relative to the location and spatial geometry of the double bond, where terminal and medial double bonds may be clearly differentiated. Figure 5 provides a good example with the spectrum of 1-hexene, which contains the terminal vinyl group. Note that a fully substituted, medial double bond has only the C=C as the sole indicator of the presence of the double bond, unless the bond is conjugated with a second unsaturated site.

Table 3 Aromatic ring (aryl) group frequencies

Origin	Group frequency, wavenumber (cm^{-1})	Assignment
C=C−C[a]	1615–1580	Aromatic ring stretch
C=C−C[a]	1510–1450	Aromatic ring stretch
C−H	3130–3070	Aromatic C−H stretch
C−H	1225–950 (several)	Aromatic C−H in-plane bend
C−H	900–670 (several)	Aromatic C−H out-of-plane bend
	770–730 + 710–690	Monosubstitution (phenyl)
	770–735	1,2-Disubstitution (ortho)
	810–750 + 900–860	1,3-Disubstitution (meta)
	860–800	1,4-Disubstitution (para)
"Combi"[b]	2000–1660 (several)	Aromatic combination bands

[a] C=C−C used as an approximation of the unique aromatic ring bonding.
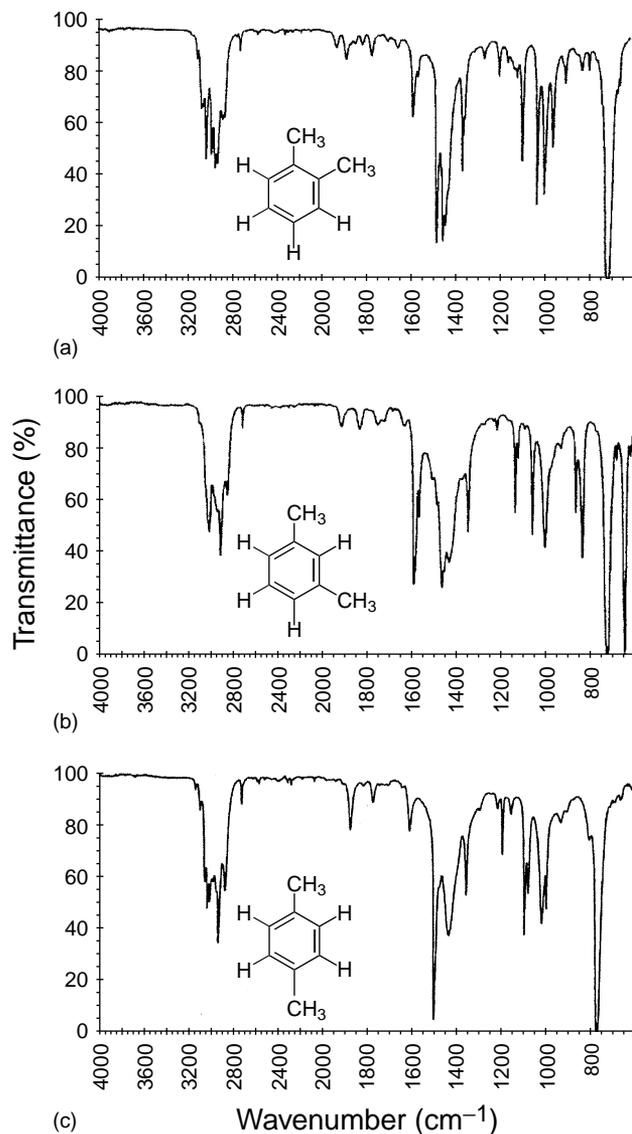[b] "Combi" denotes assignment to combination bands.

3.1.3 Aromatic Compounds

See Table 3. The existence of one or more aromatic rings in a structure is normally readily determined from the C−H and C=C−C ring-related vibrations. The C−H stretching occurs above 3000 cm^{-1} and is typically exhibited as a multiplicity of weak-to-moderate bands, compared with the aliphatic C−H stretch. The structure of the bands is defined by the number and positions of the C−H bonds around the ring, which in turn are related to the nature and number of other substituents on the ring. Note that the same applies to the C−H out-of-plane bending vibrations, which are frequently used to determine the degree and nature of substitution on the ring – examples are provided in Figure 6(a–c), with the comparison of the three xylene isomers. This picture often becomes more complex if multiple- or fused-ring structures exist in a compound. The other most important set of bands are the aromatic ring vibrations centered around 1600 and 1500 cm^{-1}, which usually appear as a pair of band structures, often with some splitting. The appearance and ratio of these band structures is strongly dependent on the position and nature of substituents on the ring.

3.1.4 Acetylenic Compounds

See Table 4. Although acetylenic compounds are not very common, the spectrum associated with the C≡C structure can be characteristic. It is instructive to note the impact on the carbon–carbon bond stretching as a function of increase in bond order for the series of single-, double-, and triple-bonded carbon:

C−C stretch: ~1350–1000 cm^{-1} (skeletal vibrations)
C=C stretch: 1680–1620 cm^{-1}
C≡C stretch: 2260–2100 cm^{-1}

Figure 6 ATR spectra of xylene isomers: (a) *o*-xylene, 1,2-dimethylbenzene; (b) *m*-xylene, 1,3-dimethylbenzene; (c) *p*-xylene, 1,4-dimethylbenzene. Copyright Coates Consulting.

Table 4 Acetylenic (alkyne) group frequencies

Origin	Group frequency, wavenumber (cm^{-1})	Assignment
C≡C	2140–2100	Terminal alkyne (monosubstituted)
C≡C	2260–2190	Medial alkyne (disubstituted)
C−H	3320–3310	Alkyne C−H stretch
C−H	680–610	Alkyne C−H bend
C−H	630 (typical)	Alkyne C−H bend

This increase in bond order produces a corresponding increase in bond strength, which in turn increases the force

constant, κ (see Equation 3), supporting the Hooke's law model described earlier.

As noted in Table 4, the position of the C≡C bond is influenced by whether the group is terminal or medial. The single hydrogen of the terminal acetylene itself is very characteristic, reflecting the labile nature of the acetylenic C−H.

3.2 Simple Functional Groups

Obviously, there is a potentially broad number of molecular fragments that can be considered to be functional groups attached to an organic structure or backbone. This section features the most simple and most common of the functional groups, −C−X, i.e. the halogens (X = F, Cl, Br and I), hydroxy (X = OH), oxy or ether (X = OR, where R = alkyl), and amino (X = NH$_2$, =NH or ≡N). With the exception of the carbonyl functionality, these three basic functional groups cover most of the common occurrences in simple organic compounds. Note that for the oxy/hydroxy and amino functionalities, these are molecular fragments, and they contribute their own set of characteristic absorptions to the spectrum of the compound. In fact, the bonding between the functional group and the backbone is only one part of the overall picture used for the spectral interpretation.

3.2.1 Halogenated Compounds

See Table 5. In principle, the interpretation of the spectra of molecules containing one or more halogens would seem to be straightforward. The functionality is simple, with just a single atom linked to carbon to form the group. With the polar nature of this group, one would expect the spectral contribution to be distinctive. In reality, this is not always the case.

In aliphatic compounds, the C−X bond typically possesses a unique group frequency, which may be

Table 5 Aliphatic organohalogen compound group frequencies

Origin	Group frequency, wavenumber (cm^{-1})[a]	Assignment
C−F	1150–1000	Aliphatic fluoro compounds, C−F stretch
C−Cl	800–700	Aliphatic chloro compounds, C−Cl stretch
C−Br	700–600	Aliphatic bromo compounds, C−Br stretch
C−I	600–500	Aliphatic iodo compounds, C−I stretch

[a] Note that the ranges quoted serve as a guide only; the actual ranges are influenced by carbon chain length, the actual number of halogen substituents, and the molecular conformations present.

assigned to the halogen–carbon stretching. When a single halogen is present, the determination of this group is straightforward. However, if more than one halogen is present, the interpretation is usually more complex. In such cases, the result varies depending on whether the halogens are on the same or different carbon atoms, and, if on different atoms, whether the atoms are close neighbors. This is particularly the case with small molecules, and the resultant spectral complexity arises from the fact that there is restricted rotation about the carbon–carbon bond.

Single bonds usually exhibit free rotation, which would normally mean that there are no preferred spatial orientations for the molecules. However, owing to the size of the halogen atom, relative to the carbon and hydrogen that form the backbone, the molecules tend to exhibit certain specific conformations, where the spatial interaction between neighboring halogen atoms is minimized, and each conformation provides its own contribution to the overall spectrum. It is important to appreciate that this issue of spatial orientation has an impact even on high-molecular-weight compounds, such as the polyhalogenated polymers, e.g. poly(vinyl chloride). Here preferred orientations have an impact on the crystallinity of the polymer, and this in turn has a significant impact on both the spectrum and the physical properties of the material.

Another important issue to consider with halogen substituents is the high electronegativity of the halogen atom. This can have a noticeable impact on the spectrum of neighboring group frequencies, including adjacent hydrogen atoms. In such cases, significant shifting of the C−H frequencies can occur – the direction of the shift being dependent on the location of the C−H, and whether the halogen adds or extracts electron density from the C−H bond – adding strengthens (higher frequency) and extracting weakens (lower frequency). The same influences can be observed with halogen-substituted carbonyl compounds, such as acyl halides and α-substituted acids, where the bond strength of the carbonyl group is increased (see section 3.3). In most cases, both a shift to higher frequency and an increase in absorption strength for the band are observed.

Table 5 only presents the group frequencies for the aliphatic compounds, because no well-defined C−X absorptions are observed for halogen-substituted aromatic compounds. The presence of a halogen on an aromatic ring can be detected indirectly from its electronic impact on the in-plane C−H bending vibrations. Normally, we do not consider the in-plane bending bands to be of use because, as pointed out earlier, these occur in a spectral region that is crowded by other important group frequencies. However, in the case of a halogen-substituted ring, the intensity of these vibrations is enhanced relative

to other absorptions by as much as three to four times. For reference, it is informative to compare the intensities for these bands, between 1150 and 1000 cm^{-1}, for the spectra of toluene and chlorobenzene (Figure 7a and b).

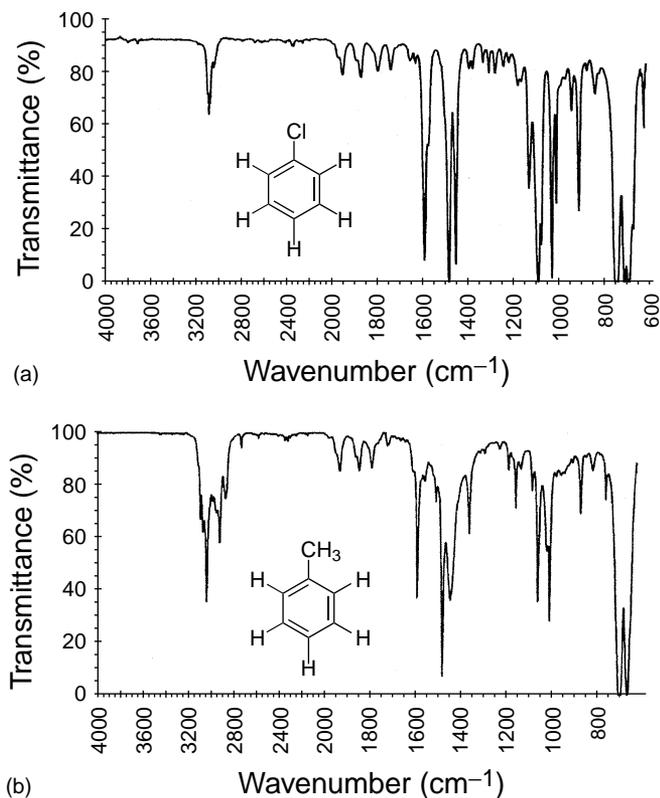### 3.2.2 Hydroxy and Ether Compounds

See Table 6 for alcohols and hydroxy compounds. The hydroxy function is probably one of the most dominant and characteristic of all of the infrared group frequencies. In most chemical environments, the hydroxy group does not exist in isolation, and a high degree of association is experienced as a result of extensive hydrogen bonding with other hydroxy groups. These hydroxy groups may be within the same molecule (intramolecular hydrogen bonding) or they most likely exist between neighboring molecules (intermolecular hydrogen bonding). The impact of hydrogen bonding is to produce significant band broadening and to lower the mean absorption frequency. The lowering of the frequency tends to be a function of the degree and strength of the hydrogen bonding. In compounds such as carboxylic acids, which exhibit extremely strong hydrogen bonding, forming a stable dimeric structure, a highly characteristic, large shift to lower frequencies is observed.

(a)

(b)

Figure 7 Comparison of ATR spectra of (a) chlorobenzene and (b) toluene. Copyright Coates Consulting.

Table 6 Alcohol and hydroxy compound group frequencies

Origin	Group frequency, wavenumber (cm^{-1})	Assignment
O−H	3570−3200 (broad)	Hydroxy group, H-bonded OH stretch
	3400−3200	Normal "polymeric" OH stretch
	3550−3450	Dimeric OH stretch
	3570−3540	Internally bonded OH stretch
O−H	3645−3600 (narrow)	Nonbonded hydroxy group, OH stretch
	3645−3630	Primary alcohol, OH stretch
	3635−3620	Secondary alcohol, OH stretch
	3620−3540	Tertiary alcohol, OH stretch
	3640−3530[a]	Phenols, OH stretch
O−H	1350−1260	Primary or secondary, OH in-plane bend
	1410−1310	Phenol or tertiary alcohol, OH bend
	720−590	Alcohol, OH out-of-plane bend
C−O	~1050[b]	Primary alcohol, C−O stretch
	~1100[b]	Secondary alcohol, C−O stretch
	~1150[b]	Tertiary alcohol, C−O stretch
	~1200[b]	Phenol, C−O stretch

[a] Frequency influenced by nature and position of other ring substituents.
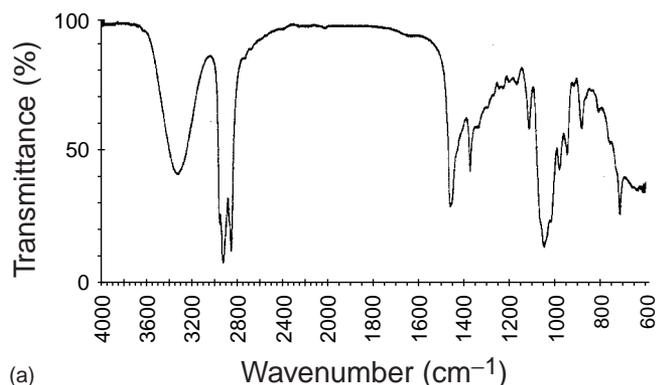[b] Approximate center of range for the group frequency.

In special circumstances, where the hydroxy group is isolated – either because of steric hindrance effects or because the sample is in the vapor state or in a dilute solution of a nonpolar solvent – the band is characteristically narrow, and is observed at the natural, higher frequency. This absorption is important for the characterization of certain hindered phenol antioxidants, a commercially important class of compounds in the food, polymer, and formulated oil industries.
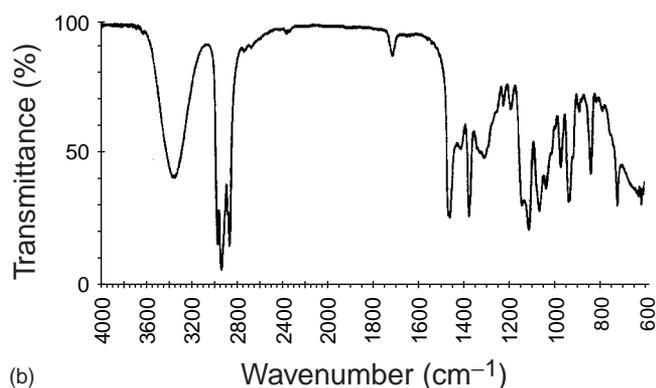
It must be appreciated that while the hydroxy absorption is singly one of the most important bands in the infrared spectrum, other vibrations are also important for the actual characterization of the compound. Alcohols exist as three distinct classes – primary, secondary and tertiary – distinguished by the degree of carbon substitution on the central hydroxy-substituted carbon, a single substitution being primary, double substitution being secondary, and triple substitution being tertiary. This is an important fact, because the chemistry and oxidation stability of the alcohol are strongly influenced by the degree of substitution. Whether an alcohol is primary (1°), secondary (2°) or tertiary (3°), may be reflected in the position of the OH stretch absorption, but typically this is determined by the other absorptions, in particular the C−O− stretching frequency. Another absorption of lower importance, but often characteristic, is assigned

to another form of bending vibration, the out-of-plane bend or wagging vibration of the O−H. The OH bending vibrations are broadened by hydrogen bonding as is the stretching absorption, but often to a lesser extent. The differences between primary and secondary alcohols can be appreciated from Figure 8(a) and (b), where the spectra of 1- and 2-octanol are presented.

See Table 7 for ethers and oxy compounds. In some respects, ethers are related to alcohol and hydroxy

Figure 8 ATR spectra of (a) primary (1-octanol) and (b) secondary (2-octanol) alcohols. Copyright Coates Consulting.

Table 7 Ether and oxy compound group frequencies

Origin	Group frequency, wavenumber (cm^{-1})	Assignment
C−H	2820–2810	Methoxy, C−H stretch (CH$_3$−O−)
C−O−C	1150–1050	Alkyl-substituted ether, C−O stretch
C−O−C	1140–1070	Cyclic ethers, large rings, C−O stretch
φ−O−H	1270–1230	Aromatic ethers, aryl−O stretch
C−O−	~1250 + 890–800[a]	Epoxy and oxirane rings
C−O−O−C	890–820[a]	Peroxides, C−O−O− stretch

[a] Typically very weak, and not very characteristic in the infrared. Tend to be more characteristic in the Raman spectrum.

compounds, where the hydrogen of the hydroxy group is replaced by an aliphatic (alkyl) or aromatic (aryl) molecular fragment. Having stated that, the overall appearance of an ether spectrum is drastically different from that of a related alcohol. This is due to the overwhelming effect of hydrogen bonding on the hydroxy group. However, many of the relationships that exist for the C−O component of the alcohol carry over to the corresponding ether. The relationships that pertain to primary, secondary, and tertiary structures remain intact. The main difference is that one now considers the bonding on both sides of the oxygen, because if carbon is on both sides, then two ether bonds exist. Ethers can exist as simple ethers (same group both sides) and mixed ethers (different groups both sides). Infrared spectroscopy is fairly sensitive for differentiating these ether functions, especially when the structures are mixed aliphatic or aliphatic/aromatic.

3.2.3 Amino Compounds

See Table 8. In some respects, the infrared spectra and the characteristic group frequencies of amines tend to

Table 8 Amine and amino compound group frequencies

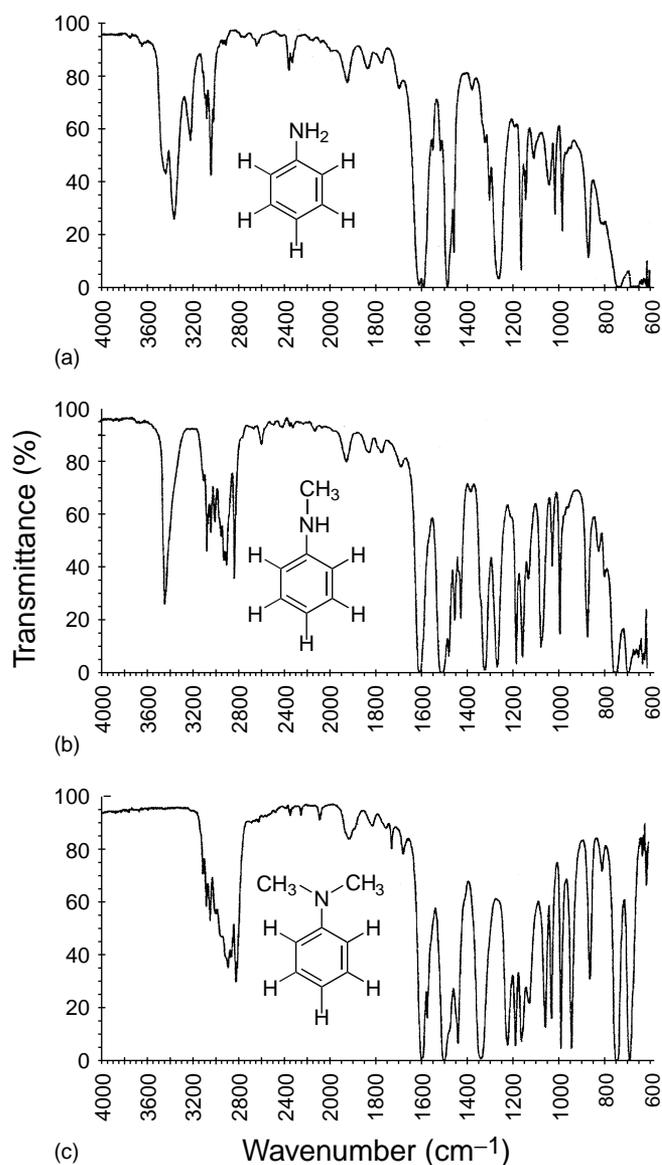| Origin	Group frequency, wavenumber (cm^{-1})	Assignment
		Primary amino
N−H	3400–3380 +3345–3325	Aliphatic primary amine, NH stretch
N−H	3510–3460 +3415–3380	Aromatic primary amine, NH stretch
N−H	1650–1590	Primary amine, NH bend
C−N	1090–1020	Primary amine, CN stretch
		Secondary amino
>N−H	3360–3310	Aliphatic secondary amine, NH stretch
>N−H	~3450	Aromatic secondary amine, NH stretch
>N−H	3490–3430	Heterocyclic amine, NH stretch
=N−H	3350–3320	Imino compounds, NH stretch
>N−H	1650–1550	Secondary amine, NH bend
C−N	1190–1130	Secondary amine, CN stretch
		Tertiary amino
C−N	1210–1150	Tertiary amine, CN stretch
		Aromatic amino
C−N	1340–1250	Aromatic primary amine, CN stretch
C−N	1350–1280	Aromatic secondary amine, CN stretch
C−N	1360–1310	Aromatic tertiary amine, CN stretch

parallel those of alcohols and ethers. Before proceeding, there is an important distinction to be made between the nomenclature used to describe alcohol structures, compared with that used for amines. The terms primary, secondary, and tertiary are used to describe amines, but the substitution relates to the nitrogen, not the adjoining carbon (as with alcohols). The terminology used is $-NH_2$ primary, $>NH$ secondary and $>N-$ tertiary. As before, these structural differences are important, and they strongly influence the chemistry and the reactivity of the nitrogen and the N−H group (primary and secondary). Again, the infrared spectrum is very diagnostic, and it is possible to differentiate readily the functional group structures, especially for the primary and secondary amino compounds (see Figure 9a–c for an example comparison of primary, secondary, and tertiary aromatic amines).

As with hydroxy compounds, hydrogen bonding is important, but the effect tends to be weaker than for the hydroxy group, and the overall effect on the spectrum is slightly less pronounced. This situation alters in the related ammonium and amino salts, where strong hydrogen bonding is experienced, and a corresponding broadening of the associated NH absorptions is observed.

Note that only the primary and secondary amines exhibit the most characteristic group frequencies, which are associated with the N−H bond. Tertiary amines are very comparable to ethers, and the main diagnostic information is gathered from the C−N vibrations only. An important exception is the methylamino (and dimethylamino) group, which like its counterpart (methoxy in ethers) has a characteristic C−H stretching vibration at lower than the normal C−H stretching frequency for methyl.

3.3 The Carbonyl Group

Carbonyl compounds are not only chemically important, but are also important in the interpretation of infrared spectra. The C=O absorption is almost always one of the most characteristic in the entire spectrum, and it is also most likely to be the most intense spectral feature. Table 9 provides an example listing of some of the common carbonyl frequencies as a function of the particular type of carbonyl group. In essence, a ketone is considered the root compound, with an aldehyde being a special case, where the carbonyl group is terminal, and only has one substituent, the other being a single hydrogen atom. All of the other carbonyl compounds, in a way, can be considered to be derived from the base ketone structure, where one or both alkyl (or aryl) substituents are replaced by another functionality, e.g. from a single hydroxy group, in the case of carboxylic acids, to two ether groups, as in the case of an organic carbonate.

Figure 9 ATR spectra of (a) primary (aniline), (b) secondary (*N*-methylaniline) and (c) tertiary (*N,N*-dimethylaniline) aromatic amines. Copyright Coates Consulting.

The actual diagnostic carbonyl absorption frequency is dependent on the electronic characteristics of the substituent group, which in turn define very much the chemical characteristics and reactivity of the specific carbonyl compound. Spatial and structural factors can be important, in particular ring stress, as in the case of lactones (cyclic esters) and lactams (cyclic amides). In this case, the greater the ring stress, the higher is the carbonyl absorption frequency. In common with previous observations for a double-bonded functionality, conjugation plays an important role in the observed carbonyl frequency. This includes connection to an aromatic ring or conjugation to a C=C or another C=O.

Table 9 Example carbonyl compound group frequencies

Group frequency (cm^{-1})	Functional group
1610–1550/1420–1300	Carboxylate (carboxylic acid salt)
1680–1630	Amide
1690–1675/(1650–1600)[a]	Quinone or conjugated ketone
1725–1700	Carboxylic acid
1725–1705	Ketone
1740–1725/(2800–2700)[b]	Aldehyde
1750–1725	Ester
1735	Six-membered ring lactone
1760–1740	Alkyl carbonate
1815–1770	Acid (acyl) halide
1820–1775	Aryl carbonate
1850–1800/1790–1740	Open-chain acid anhydride
1870–1820/1800–1775	Five-membered ring anhydride
2100–1800	Transition metal carbonyls

[a] Lower frequency band is from the conjugated double bond.
[b] Higher frequency band characteristic of aldehydes, associated with the terminal aldehydic C−H stretch.

As previously discussed, a lowering of the parent group frequency is observed. This effect is important for the differentiation of certain types of carbonyl compound, in the determination of whether the carbonyl group is directly or indirectly attached an aromatic ring, e.g. the ability to differentiate aryl acetates from alkyl benzoates. In the case of the acetate, the ring is joined to the "ether oxygen" of the ester group, and is not conjugated with the carbonyl, whereas with the benzoate, the ring is directly conjugated with the group, and the carbonyl absorption frequency is correspondingly lowered.

Often, the frequency ranges for the different classes of carbonyl compound overlap, and the carbonyl frequency alone is not sufficient to characterize the functional group. In most cases, spectral information from the other component of the functional group is used for the characterization. Carboxylic acids are a good example, where the C−O, C−O−H and O−H vibrations are highly characteristic. Similarly, esters (C−O−C) and amides (C−N and N−H) are other frequently encountered examples. The frequencies provided earlier for these additional functionalities (C−O, C−N, and N−H) in general apply, although the actual observed frequencies may differ slightly, being modified by the carbonyl group. It is worthwhile returning momentarily to carboxylic acids, because they are unique, in so far as the hydroxy group has direct interaction with the carbonyl group, by the formation of a stable dimeric hydrogen-bonded structure in the condensed phase (solid and liquid). Note that this structure disappears in the vapor state. A characteristic broad feature in the range 3300–2500 cm^{-1}, that overlaps the C−H stretching region, and with a secondary absorption close to 2600 cm^{-1}, is observed for
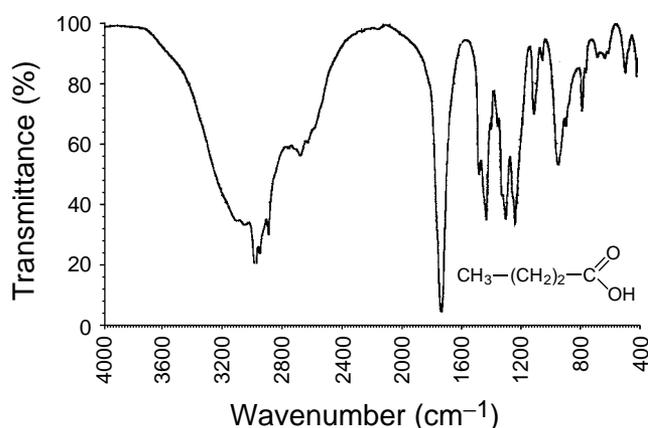
the hydrogen-bonded O−H of most carboxylic acids. The impact of this overlap can be appreciated by reference to the spectrum of butyric acid, provided in Figure 10. Other bands that are associated with the C−O and O−H components tend to be less pronounced, and sometimes may be overlapped with other fingerprint absorptions of the molecule. These are located in the ranges 1320–1210 cm^{-1} (C−O stretch) and 960–850 cm^{-1} (hydrogen-bonded O−H out-of-plane bending).

3.4 Other Functional Groups Associated with Heteroatoms

Potentially there are very large numbers of different organic-based compounds that are associated with one or more heteroatoms. These are in addition to the simple halogen- and amino-based compounds that have already been covered. A detailed discussion of such compounds is beyond the scope of this article. A few illustrative examples are included here in order to provide the reader with a feel for the spectral contributions of commonly encountered compounds that feature heteroatoms. These include triple-bonded and cumulated double-bonded nitrogen compounds, such as cyano and cyanato compounds, hetero-oxy compounds, such as nitro, sulfoxy, phosphoroxy and silicoxy compounds, and thiols and thio-substituted compounds. Many of these belong to important compound classes, and complete texts exist that focus on the spectral attributes of such compounds.

3.4.1 Multiple-bonded and Cumulated Double-bonded Nitrogen Compounds

Nitrogen compounds featuring triple or cumulated double bonds, such as cyanides or nitriles (−C≡N) and cyanates (−O−C≡N), all provide a unique spectrum, typically with a single, normally intense absorption at 2280–2200 cm^{-1}

Figure 10 Transmission spectrum of *n*-butyric acid. Copyright Coates Consulting.

(for cyano compounds) and 2285–1990 cm^{-1} (cyanates, isocyanates, thiocyanates, etc.). The band is assigned to the stretching vibration, which is the asymmetric stretch in the case of the cumulated double-bonded compounds (the symmetric stretch is typically weak, and is not diagnostic of the group).

Double-bonded nitrogen groups, such as imino groups ($>$C=N$-$) and azo groups ($-$N=N$-$), exhibit absorptions close to the carbonyl (C=O) and alkene (C=C) double bond stretching region. While they are characteristic for the functional group, they are sometimes difficult to assign from first principles because of the overlap with other common functional groups in the region. For example, dependent on substitution or location, the $>$C=N$-$ group can occur in the same spectral region as the C=O of an amide. Examples of the group frequencies for a few common multiple-bonded and cumulated double-bonded compounds are provided in Table 10.

3.4.2 Hetero-oxy Compounds

The group of compounds covered here feature X$-$O (where X = nitrogen, sulfur, phosphorus, and silicon) and X=O vibrations. In general, the characteristic absorptions span a similar range to that covered by the corresponding carbon–oxygen compounds, with most of the stretching frequencies observed within the main fingerprint spectral region (1500–400 cm^{-1}). Many of the compounds can be considered to be analogs of ethers, especially when an alkoxy group is present, featuring the X$-$O$-$C linkage. Interestingly, the nitro group ($-$NO$_2$) is isoelectronic with the carboxylate ion group ($-$CO$_2{}^-$), and both provide very similar spectra for the main functional group. See Table 11 for example group frequencies for hetero-oxy compounds.

3.4.3 Thiols and Thio-substituted Compounds

Thiols and thio-substituted compounds, by definition, can be considered to be the direct analogs of the equivalent

Table 10 Examples of nitrogen multiple and cumulated double bond compound group frequencies

Group frequency (cm^{-1})	Functional group/assignment
2280–2240	Aliphatic cyanide/nitrile
2240–2220	Aromatic cyanide/nitrile
2260–2240/1190–1080	Cyanate ($-$OCN and C$-$OCN stretch)
2276–2240	Isocyanate ($-$N=C=O asym. stretch)
2175–2140	Thiocyanate ($-$SCN)
2150–1990	Isothiocyanate ($-$NCS)
1690–1590	Open-chain imino ($-$C=N$-$)
1630–1575	Open-chain azo ($-$N=N$-$)

Table 11 Example group frequencies for simple hetero-oxy compounds

Group frequency (cm^{-1})	Functional group/assignment
Nitrogen-oxy compounds	
1560–1540/1380–1350[a]	Aliphatic nitro compounds
1555–1485/1355–1320[a]	Aromatic nitro compounds
1640–1620/1285–1270[a]	Organic nitrates
Phosphorus-oxy compounds	
1350–1250	Organic phosphates (P=O stretch)
1050–990	Aliphatic phosphates (P$-$O$-$C stretch)
1240–1190/995–850	Aromatic phosphates (P$-$O$-$C stretch)
Sulfur-oxy compounds	
1335–1300/1170–1135[a]	Dialkyl/aryl sulfones
1420–1370/1200–1180[a]	Organic sulfates
1365–1340/1200–1100[a]	Sulfonates
Silicon-oxy compounds	
1095–1075/1055–1020	Organic siloxane or silicone (Si$-$O$-$Si)
1110–1080	Organic siloxane or silicone (Si$-$O$-$C)

[a] Asymmetric/symmetric XO$_2$ stretch (NO$_2$ and SO$_2$).

oxygenated compounds such as alcohols and ethers. Unlike the oxygen-containing analogs, the equivalent C$-$S and C$-$S$-$H stretching vibrations tend to give rise to very weak absorptions in the infrared spectrum. The C$-$S and S$-$H bonds are highly polarizable, and hence produce stronger spectral activity in the Raman spectrum than the infrared spectrum. The higher mass of sulfur, compared with oxygen, results in the characteristic group frequencies occurring at noticeably lower frequencies than the oxygen-containing analogs, as noted in Table 12 for compounds containing S$-$H and C$-$S bonds. The thiol S$-$H is probably the only infrared absorption that can be considered to be of use for the general characterization of these compounds, and most of the others are obtained by inference, or from knowledge of the compound type. Catenation is a unique chemical characteristic of sulfur, where the formation of S$-$S bonds in extended chains is common, hence the inclusion here of the S$-$S stretching frequencies.

3.5 Simple Inorganics

Characterization of compounds via infrared spectroscopy is not limited to organic compounds. Any inorganic compound that forms bonds of a covalent nature within a molecular ion fragment, cation or anion, will produce a characteristic absorption spectrum, with associated group frequencies. In a manner, certain aspects

Table 12 Common group frequencies for thiols and thio-substituted compounds

Group frequency (cm^{-1})	Functional group/assignment
2600–2550	Thiols (S−H stretch)
710–685	Thiol or thioether, CH_2−S− (C−S stretch)
660–630	Thioethers, CH_3−S− (C−S stretch)
715–670	Aryl thioethers, ϕ−S (C−S stretch)
705–570	Disulfides (C−S stretch)
620–600	Disulfides (S−S stretch)
500–430	Aryl disulfides (S−S stretch)
500–470	Polysulfides (S−S stretch)

Table 13 Example group frequencies for common inorganic ions

Group frequency (cm^{-1})	Functional group/assignment
1490–1410/880–860[a]	Carbonate ion
1130–1080/680–610[a]	Sulfate ion
1380–1350/840–815[a]	Nitrate ion
1100–1000	Phosphate ion
1100–900	Silicate ion
3300–3030/1430–1390[a]	Ammonium ion
2200–2000	Cyanide ion, thiocyanate ion, and related ions

[a] Typically, the first absorption is intense and broad, and the second has weak to medium intensity and is narrow. Both often exist as multiple band structures, and this may be used to characterize individual compounds.

have already been covered for inorganic compounds in the form of salts of carboxylic acids and amino and ammonium compounds, which can be extended to metal complexes, chemical fragments associated with hetero-oxy groups (nitrates, sulfates, phosphates, silicates, etc.), and transition metal carbonyl compounds. All complex ionic compounds (containing more than one atom) and coordination compounds produce characteristic spectra. Many of the associated group frequencies can be used diagnostically for characterization. The structure and orientation of the ion or complex, both as an isolated entity or within a crystal lattice, are important factors that affect the appearance and nature of the infrared spectrum. Hydration of compounds (water of crystallization) also has a large effect on the spectrum, and often adds a lot of complexity, in the form of additional absorption bands and structure to existing bands. The subject is far too broad to be covered in this article, and only a few example group frequencies are included here (Table 13). The reader is directed to the recommended standard texts for more detailed information.[13,14]

4 THE PRACTICAL SITUATION – OBTAINING THE SPECTRUM AND INTERPRETING THE RESULTS

Up to this point, the fundamentals of interpretation have been discussed from the most basic concepts of infrared absorption by a molecular species and the impact of chemical functionality on the resultant spectrum. In many ways, this discussion has treated the molecule as a more or less isolated species, with no consideration of the physical state of the actual sample or the environment in which the molecule exists. Physical state and the molecular, chemical and physical environments have a profound effect on the infrared spectrum. As a result, it is just as important to understand and interpret these effects as it is to perform the fundamental interpretation of the functional groups from first principles.

This particular section may be one of the most important for many of the readers, because it reflects the real world, that is taking a sample, preparing it for analysis, and making use of all of the available information on the sample and the spectrum or spectra obtained. Note that sometimes there are several options in the way that a sample may be handled for infrared analysis. It is often beneficial to consider the different options. Before we start to examine the situation it is important to understand the importance of the interpretation and to determine the real requirements. Here are some example scenarios:

1. The sample (or spectrum) is a "total unknown" and an identification is required – examples include forensic samples, environmental waste samples, or new discovery samples, where a new material has been synthesized or discovered.

2. The sample (or spectrum) is an unknown and it needs to be characterized or classified – examples include commercial applications where new additives or components are included in a material to provide a specific property; in such cases this could be considered the basis of competitive product analysis.

3. The sample generally is known but the existence of a specific chemical class needs to be determined – examples include contaminant analysis, analysis for toxicology or environmental reasons, material additives, etc.

4. The sample is a complete known and the interpretation is required to confirm the material composition and/or quality – examples include product quality control and the confirmation of a structure or functionality of a newly synthesized material.

There are clearly many other scenarios that can be considered, and the examples presented may cross over into more than one of these scenarios. However, the idea here is to help define a strategy for the interpretation. For the most part, this text will focus on scenarios 1 and 2, although a passing reference may be made to the others. Note also that there are two ways to address the interpretation:

- one is to attempt to assign as many bands as possible using group frequency tables;

- the other is to attempt to build up a picture using information from key spectral bands (with a knowledge of the group frequencies) and rationalizing the spectrum relative to the sample as known, and any known history, including the sample preparation and presentation technique.

The latter approach is the best way to go, and is typically far more rewarding. Also, it is seldom that all bands in the infrared spectrum of a sample can be fully or accurately assigned. There are too many ambiguities and coincidences for a definitive interpretation to be obtained from the spectra of most materials – remembering, of course, that the sample may be a mixture.

To begin, let us start from either the point where a spectrum has been generated or where a sample is presented. In practice, these are very different starting points. The latter is always preferred because with the sample in hand it is possible to gain a lot of first-hand information about nature which will ultimately help in the final interpretation. The term ''unknown'' is used because this is how people often view the interpretation process; however, in reality there are seldom true unknowns – in other words, the reason for the interpretation itself often provides implied information about the sample. Even if a person presents a prerecorded spectrum, it is usually accompanied by some additional information. This at minimum should include a knowledge of how the sample was prepared, whether it is a solid, liquid, or gas, or some mixed state, and maybe some physical characteristics (color, appearance, melting point/boiling point, etc.). For the benefit of presenting a complete picture, we shall assume that the sample is available and that we have the opportunity to perform additional tests and measurements on it. Further, more detailed discussions of this practical approach can be found in the literature.[18–20]

4.1 Sample History

As noted, we are seldom dealing with a true unknown, and typical situations include the following:

- a sample of fiber taken or extracted from a particular environment;
- a contaminant removed from a material;
- a suspicious liquid found leaking out of some drums;
- a residue extracted from a surface;
- a residual liquid or solid remaining after storage or treatment of a product;
- extracted additives or components from a commercial product;
- a mass that was produced after a specific chemical reaction;
- or simply a manufactured product.

Most people can equate with these different sets of circumstances. Each one brings information about the sample.

In the case of a fiber, if it is organic, then it typically fits within certain classes of polymeric materials. It may have orientation properties, which will influence the appearance of the infrared spectrum, depending on how it is sampled, and if there is more than one fiber, then the original material may have been a blend. The environment from where the sample was taken will be important because there may be surface contaminants that may produce spurious bands in the spectrum, which may be removed by some sample pretreatment, such as washing with a solvent. Alternatively, the fiber may be coated, or degraded, thermally or by oxidation.

The characterization of contaminants is a common application for infrared spectroscopy. For this type of exercise it is necessary to know the importance of the contaminant and why it is believed to be a contaminant. Was it extracted from a liquid or solid matrix? if so, what type of matrix, and what was the composition of the matrix? Is it possible that the contaminant originated from the matrix itself, as a breakdown product? – if so, then there should be some chemical similarities or common heritage. Was it embedded within a matrix, such as a plastic/polymer film or a sheet of paper? – if so, is the contaminant itself potentially contaminated by the matrix? This is especially important for interpretation, because the matrix may have a very intense infrared spectrum of its own.

For extracted materials, such as additives removed from a polymer, it is important to know something about the polymer matrix – few extractions are 100% efficient, and it is common to have carry-over. In many such cases, the spectrum obtained reflects that of a mixture rather than a pure compound. Things to bear in mind here are what the original base polymers were, what other additives could be present, and what material, usually a solvent, was used for the extraction.

Looking at residues and residual products of a reaction is similar to the concept of characterizing a contaminant. Residues formed within products are often the result of a breakdown reaction or an unexpected interaction between components. If derived from one or more of the components, then a knowledge of all of the ingredients is essential – again we would be looking for chemically related species in the residue, and reference spectra of each of the ingredients would be important in attempting to characterize the material. In the case of a reaction product, spectra for the reactants and any solvents or substrates (catalysts, etc.) used would be helpful.

Finally, the identification of an end product from its infrared spectrum is common practice. By definition, unless the final product is a pure chemical, most manufactured products are mixtures, often featuring blended solid and/or liquid components from percentage range concentrations to trace amounts. Often at issue is how much can be identified from the interpretation of a single spectrum. It is often necessary to perform some form of preconcentration on one or more ingredients, or to perform a chemical modification to change the spectral response of one or more of the major ingredients. This latter operation may help to remove the spectral interferences from a major component for determining the presence of minor components.

4.2 Physical Characteristics of the Sample

From considerations based on the discussions in the section above, a good working knowledge of the sample allows one to determine basic information about the sample. This information can help in the determination of the best method of sampling. It can also help to indicate if any special treatments to the sample are necessary before proceeding, such as the removal of residual solvents, or the need for selective extraction, in the event that the sample has more than one phase, or is known to be a mixture. Beyond this there are other important physical characteristics of the sample that can assist the interpretation process. As indicated, physical state can be very important. For example, it has been noted that nitro compounds are isoelectronic with organic acid salts. Many simple nitro compounds are liquids, whereas simple carboxylates are usually solids.

There are, however, many other physical characteristics and attributes that can be linked to the sample and its chemistry. This in turn can be linked to important spectral features in the infrared spectrum. Two important characteristics are color and odor. Nitrogen compounds often have color associated with them, e.g. nitro-substituted compounds often have a characteristic yellow or orange color, especially substituted phenols and amines. Similarly, unsaturated nitrogen compounds, such as azo

compounds, and highly conjugated olefinic compounds, such as carotenes, are similarly colored. This can be used as a guide to look for the specific functionality in the spectrum.

Likewise, odor can be a useful guide. This author is not advocating that a person should inhale the vapor of a sample directly, for obvious reasons. However, if under cautious sampling conditions a characteristic odor is detected, then this can provide a valuable insight regarding the presence of particular functional groups. Common examples are alcohols, esters, and ketones, which often possess relatively pleasant fragrances, especially when associated with some degree of unsaturation. An almond-like odor might indicate a nitro compound, benzaldehyde, or a cyano compound (caution!), a fish-like odor is often associated with amino or amido compounds, and a putrid or "bad-cheese" odor is associated with certain carboxylic acids. With time, one can build up a mental library of common odors and fragrances, and these can be very valuable for initial material screening, by helping one look for the presence of specific functional groups.

Volatility and flammability can be useful guides. Most volatile compounds tend to have a relatively low molecular weight, and they usually are unassociated. This latter point helps to rule out certain hydrogen-bonded species, such as carboxylic acids, amines, and multiple hydroxy-substituted compounds (such as glycols). If a sample is submitted for some form of combustion analysis, it is worthwhile monitoring how it burns. If it burns with a clean, bluish flame, that might indicate that the sample is oxygenated (alcohol or ether). If it has a yellow and/or smoky flame, it indicates an excess of carbon, possible unsaturation or an aromatic compound. The latter can produce a very smoky flame.

4.3 The Chemistry of the Sample

First, there are issues relating to solubility. The old adage, like dissolves like, is very appropriate. Nonpolar materials such as hydrocarbons tend to be more soluble in nonpolar solvents, such as hydrocarbons or chlorinated solvents, whereas polar materials favor solvents such as methanol and acetone, and in extreme cases their solubility may be limited to the most polar solvents, such as water. If a material is potentially identified from its infrared spectrum as a carboxylic acid or an amino compound, then it is worthwhile to check the pH. Also, it is worthwhile to check its ability to form a salt – carboxylic acids react with sodium carbonate or sodium hydroxide to form a carboxylate salt, and amines react with dilute mineral acids, such as hydrochloric acid, to form amine salts (amine hydrochlorides with hydrochloric acid).

Certain compounds react with water; examples are acid halides and acid anhydrides. Alternatively, these

compounds will react with alcohols and amines to form esters and amides. The formation of such derivatives is common practice in the identification of organic compounds, and can be extremely informative in a definitive identification by infrared spectroscopy. Other chemical modifications that can be equally informative are for the identification of olefinic or unsaturated compounds. A simple reaction with bromine (caution – use in solution, or prepare in situ) will often confirm the presence of a double bond. The reaction product can be helpful in characterizing the nature of the unsaturation, especially in the case of a *cis* configuration, which is often spectrally masked by other absorptions in the region.

One similar modification, which is strictly not chemical in nature, is deuterium exchange. In this case, a compound with either a labile hydroxy group or an amino group is placed in equilibrium with a deuterated solvent, such as deuterium oxide (heavy water). The replacement of the $O-H$ in the molecule by $O-D$, in the case of hydroxy compounds, can help in the confirmation of the hydroxy group, and it can shift an overlapping hydroxy function from the $C-H$ stretching and bending regions, thereby assisting in the determination of the backbone structure. Note that the shift induced by the replacement of $O-H$ by $O-D$ is nearly as much as $1000\,cm^{-1}$.

Finally, an important chemical characteristic to be understood is hydrogen bonding. The infrared spectrum is a wonderful tool for helping to monitor the presence of this phenomenon. However, one must be aware of the fact that hydrogen bonding is usually concentration dependent. If a hydroxy compound is examined in a nonpolar solvent, one should be aware that the hydroxy group spectrum, in particular bands assigned to the stretching vibration, will change shape, position, and intensity as a function of concentration. Also, diagnostically, if the hydroxy group bands do not change significantly with concentration, then this is a strong indication of intramolecular (internal) hydrogen bonding. This latter information is important in helping to determine the spatial relationships of hydroxy groups within a molecule.

The last two sections might seem to be obvious basic knowledge in the chemistry and physical properties of a material. However, just simple observations of the type described can be invaluable in determining the presence of specific functional groups when used in combination with the infrared spectrum. Likewise, the use of negative spectral information, viz. the absence of a characteristic group frequency, is equally important. For example, if a sample has an almond-like odor, but does not have a strong band between 2200 and $2000\,cm^{-1}$, then the compound is more likely to be a nitro compound or benzaldehyde than a cyano compound. If an aldehydic carbonyl group is absent, then the compound probably contains a nitro group.

4.4 The Infrared Sampling Method

The final appearance of the infrared spectrum is very important in the interpretation process. Where possible, it always helps to be able to study the sample as it occurs naturally, without any form of physical modification. This eliminates the possibility of any interactions, or even chemical modifications. A common method for handling solid samples is known as the compressed alkali metal halide pellet method (KBr pellet or disk method). This method of sample preparation is prone to difficulties, and it often requires a skilled operator to produce good-quality spectra on a routine basis. A poor sampling technique with this method can lead to spectral artifacts and distortions, all of which can cause difficulties in the interpretation. Furthermore, some compounds may react with KBr, causing either a liberation of the halogen (oxidants) or halogen exchange (halide salts). The act of applying pressure can also change the appearance of the spectrum, especially when a material exists in more than one polymorphic form. The pressure may cause one polymorph to dominate, thereby changing the entire absorption band distribution of the spectrum. This is especially a problem with certain pharmaceutical products.

Other pretreatment methods, such as melts and cast films for solid samples, can cause similar problems. The cooling process (from melts) or the casting process can induce preferential crystallization of a particular form of the material, and sometimes preferred orientations can result. All of these effects can give rise to nonrepresentative spectra, which can cause interpretation problems.

With liquids, it is always beneficial to examine the sample as it is received. Liquid transmission cells have been used successfully in the past, but care and attention must be paid to the nature of the window material and to the cell pathlength. Low-molecular-weight materials usually require very short pathlengths in order to obtain a good-quality spectrum with most of the absorption bands on-scale. If too many bands bottom out, it is difficult to ascertain the relative intensity of certain key functional groups, and sometimes key factors, such as band splitting, may be missed. Also, if the sample is of low molecular weight, and volatile, it is important to ensure that the cell seals adequately.

In recent years, focus has been placed on reflectance methods of measurement, primarily from the surface of a sample. The most common methods are diffuse reflectance, specular reflectance and/or transflectance, and ATR. Generally, these are nondestructive methods, and require only a minimum amount of sample

preparation. The specular and transflectance methods have found greatest use with microscope-based methods of spectral measurement. Diffuse reflectance and ATR are important laboratory methods, and both lend themselves to rapid and reproducible sampling. However, both methods have an impact on the spectrum, and neither method necessarily provides a true spectrum of the sample free from some form of distortion or aberration. ATR is the simplest to handle, and its main limitation is that it provides a spectrum where the spectrum intensity across the spectrum increases as a function of wavelength. Both diffuse reflectance and specular reflectance can be the most difficult to handle, because both methods can cause severe band distortions, linked to surface and refractive index phenomena. In all three cases, the nature and the origin of the distortions are understood, and can be assigned to known physical properties. If necessary, software algorithms can be applied to correct for most of the distortions – a wavelength correction function in the case of ATR (for qualitative use), and a spectrum transformation, known as the Kramers–Kronig transform, in the case of surface reflectance distortions.

One other technique that is not so common but is important for certain "difficult-to-handle" samples is photoacoustic spectroscopy. The accessory, which also functions as the detector, provides a true absorption spectrum from a sample directly, with no sample modification. It is particularly good for samples that naturally have high absorption, such as carbon-filled materials, and for materials that are a good thermal conductor. As with ATR spectra, there is a wavelength dependence of the peak intensity across the spectrum.

The entire subject of sample handling is very broad, and generally falls outside the scope of this article. However, its impact on the final infrared spectrum and its resultant impact on the interpretation process can be very profound. Therefore, the reader is encouraged to read specific texts that address the subject in greater detail.[21–23]

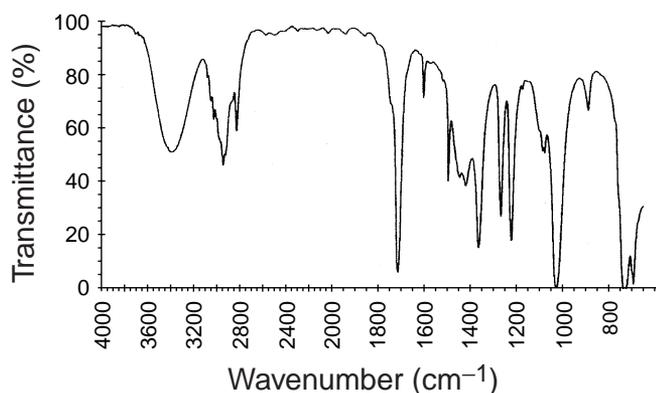# 5 AN OVERVIEW TO INFRARED SPECTRAL INTERPRETATION – SOME SIMPLE RULES AND GUIDELINES

This final section is a review of the ideas presented so far as to how to go about the interpretation of an infrared spectrum. With it, there is the implied understanding that the infrared spectrum is only one source of information, and additional information is most likely required for a satisfactory analysis of the spectrum. The following are a set of simple guidelines to help a person through the early stages of rationalizing an infrared spectrum and to get to the first stages of an interpretation. However, note that this is not a definitive set of rules.

First, it is important to appreciate that there are often recurring patterns in the spectrum that are characteristic of certain classes or compounds and/or functional groups. Such patterns can be far more diagnostic in the interpretation process than merely isolated group frequencies. Examples include the overall appearance of the hydrogen-bonded hydroxy functionality, the patterns associated with unsaturation and aromaticity, and the combinations of bands used to characterize different carbonyl compounds. To start, it is worthwhile to determine if the compound is organic (evidence of C−H functionality) and if there is a characteristic chain or ring associated with the compound. Having determined this, it is worthwhile to reflect on the complexity of the spectrum, and to see if one or two characteristic functionalities, associated with simple functional groups (−OH, −NH, C=O, etc.) are present. Often, the like-to-like rule applies – that is, a simple spectrum is usually indicative of a simple molecular structure, and vice versa.

If the spectrum clearly indicates multiple functionality, then be aware that mutual interaction may be occurring, and this may be causing some deviations from ideality, relative to the common group frequency assignments. Also, remember that multiple functionality might reflect a complex structure, but it might also reflect that the sample is a mixture. In both cases, an appreciation of the existence of spectral coincidences is very important. For example, a strong absorption between 1250 and 1150 cm^{-1} can be assigned to numerous types of chemical bonds, from the C−F group to the Si−O group. A careful assessment of the other spectral features, and most likely an understanding of the nature of the sample, will usually help in resolving some of these spectral coincidence situations. The use of known relative band intensities for certain functional groups can also be helpful in determining whether band overlap is occurring, and in particular whether the bands from a group are being obscured by other more intense bands. A good example is the overlap of the *cis* C−H out-of-plane bending vibration, which is typically overlapped by the −$(CH_2)_n$− rocking vibration of long-chain aliphatic compounds.

Also, if multiple functionality exists, some form of separation scheme may be in order to help determine if the sample is a mixture and, if so, to help separate some of the components. While this may not always be necessary – there are many commercial mixtures identifiable from the original spectrum – it is often required for a more definitive evaluation of a sample from its infrared spectrum. An example of such a mixture is provided in Figure 11. The spectrum of this four-component mixture can be interpreted from a knowledge of the components – acetone, methanol, dichloromethane

Figure 11 ATR spectrum of a commercial solvent mixture containing methanol, dichloromethane, toluene and acetone. Copyright Coates Consulting.

and toluene. However, the use of separation techniques, such as water-based solvent extraction, and partial distillation can help in determining the identity of the components.

Finally, in terms of using the first-assessment rules outlined in the remainder of this section, it is important to incorporate all known chemical and physical information, including pertinent test data, such as the presence of unsaturation, which may be used to corroborate the spectral data for a suspected double bond. Remember that simple information, such as color and odor, can be equally important – highly conjugated compounds and nitro compounds often give rise to significant color, and numerous functional groups, such as esters, ketones, unsaturation, and nitro groups, have highly characteristic fragrances or odors, even in the solid state.

The following first assessment guide is based on the examination of critical spectral regions for evidence of highly characteristic molecular backbones or fragments and functional groups. An important point to remember here is that negative information, in the form of no-band regions, is extremely important, and helps to eliminate major classes of chemical compounds, thereby reducing the number of possibilities in the final interpretation.

5.1 A Quick Diagnostic Assessment of an Infrared Spectrum

5.1.1 Step 1: Overall Spectrum Appearance

Is the spectrum simple? Are there only a few main characteristic absorption bands, say less than five?

If the spectrum is simple, as defined, then the compound may be a low-molecular-weight organic or inorganic compound, such as a simple salt of a common

molecular ion (carbonate, sulfate, nitrate, ammonium, etc.) or a covalent species (chloroform, dichloromethane, methanol, water, etc.). In this case, the physical properties are important – if the material is a crystalline solid, then it is most likely a salt; if it is a mobile, possibly volatile, liquid, then the latter probably applies. Note that there are always exceptions, e.g. bromoform and iodoform, simple covalent compounds, are crystalline solids (both melt at low temperatures, whereas salts do not). One other class of compounds worth mentioning here is simple polymers, such as polyethylene and polytetrafluoroethylene, both of which exhibit very simple spectra when obtained from thin films.

Are some of the bands broad? Hydrogen bonding possibly exists and can be exhibited in hydrates, water solutions, alcohols, ammonium compounds, amino compounds, etc. Note that some inorganics may exhibit a combination of both broad and very narrow bands, even for certain hydrated species. These are often related to the crystalline structure of the compound and the symmetry of certain aspects of the molecular/ionic structure.

5.1.2 Diagnostic Step 2: Testing for Organics and Hydrocarbons – Absorptions in the Region 3200–2700 cm⁻¹

Well-defined and characteristic absorptions in this region are normally characteristic of carbon- and hydrogen-containing species, and are assigned to various forms of C−H stretching.

Are there absorptions above 3000 cm⁻¹? If yes, then the compound is likely to be unsaturated (contains C=C) or aromatic. If isolated absorptions occur at 3010 and/or 3040 cm⁻¹, then the absorbing species is mostly simple olefinic unsaturation.

Is the main absorption below 3000 cm⁻¹? If so, the compound is probably aliphatic. If the main absorptions are approximately 2935 and 2860 cm⁻¹, and there are also absorptions at 1470 and 720 cm⁻¹, then the compound probably contains a long linear aliphatic chain.

5.1.3 Diagnostic Step 3: Testing for Hydroxy or Amino Groups – Absorptions in the Region 3650–3250 cm⁻¹

Hydroxy or amino groups mainly dominate this region, both giving rise to very characteristic band profiles. The presence or absence of hydrogen bonding is well delineated in this region. One other characteristic vibration that is observed in this region, which is unlikely to be confused with any other functional group, is the C−H stretch of a terminal alkyne (acetylenic compound). This exhibits a relatively narrow absorption at

$3300\,\text{cm}^{-1}$, and is associated with a second ($C{\equiv}C$) band at $2200\,\text{cm}^{-1}$.

Is the main absorption band in the area broad? If so, the compound is probably a hydroxy or amino group. Knowledge of the presence of nitrogen or a nitrogenous base (pH or titration) helps to support an amino compound.

Are there additional moderate to intense bands in the ranges 1600–1300, 1200–1000 and 800–600 cm^{-1}? If so, the compound is likely to be a simple hydroxy compound. Remember that the simple hydrogen-bonded OH absorption of a hydroxy (alcohol) function has a very characteristic shape.

If the feature is relatively sharp and occurs between 3670 and 3550 cm^{-1}, the compound probably contains a non-hydrogen-bonded hydroxy group, often an alcohol or phenol with a sterically hindered OH group. Note also that this spectral feature is also exhibited by certain inorganics and minerals, and is indicative of a "free" OH group, either on the surface, or embedded within a crystal lattice, and free from interactions with other ions or groups.

5.1.4 Diagnostic Step 4: Testing for Carbonyl Compounds – Absorptions in the Region 1850–1650 cm^{-1}

A major band in this region usually indicates the presence of a $C{=}O$ group (carbonyl compound). Note that certain $C{=}N$ (imino) and $N{=}N$ (azo) groups may interfere, example compounds being purines.

Is the absorption at the high end of the range, e.g. $1775\,\text{cm}^{-1}$ or above? If yes, the compound probably contains a reactive carbonyl, such as an anhydride, acid halide (acyl halide) or α-halogenated carbonyl, or a strained-ring carbonyl, such as a lactone, or an organic carbonate.

Is the absorption in the middle of the range, 1750–1700 cm^{-1}? If yes, the compound is probably a simple carbonyl compound, such as a ketone, an aldehyde, an ester, or a carboxylic acid.

Is the absorption at the low end of the range, e.g. below $1700\,\text{cm}^{-1}$? If yes, the compound is probably an amide or a carboxylate (carboxylic acid salt). Note that conjugation with another carbonyl group, or a double bond or aromatic ring, will lower the carbonyl absorption by 30–50 cm^{-1}. Therefore, conjugated aldehydes, ketones, esters, and carboxylic acids may fall into this lower end category. If conjugation with a double bond is present, then a second strong absorption should be observed nearby, between 1650 and 1600 cm^{-1}. In the case of the involvement of an aromatic ring, it is important to look for evidence of the characteristic aromatic absorptions (see Diagnostic Step 6).

5.1.5 Diagnostic Step 5: Testing for Unsaturation – Weak to Moderate Absorption in the Region 1670–1620 cm^{-1}

Note that this is not a particularly definitive diagnostic without the support of other corroborating absorptions.

A relatively narrow, weak-to-moderate absorption, normally centered around $1650\,\text{cm}^{-1}$, is indicative of olefinic unsaturation ($C{=}C$). A lowering of this frequency, accompanied by intensification of the band, is characteristic of conjugation with another double bond structure, such as $C{=}C$, $C{=}O$ or an aromatic ring (see comments in Diagnostic Step 4).

The test for unsaturation normally involves a check for $C{-}H$ peaks above $3000\,\text{cm}^{-1}$, and typically as a single, or possibly a pair, of absorptions (dependent on configuration of the double bond) at $\sim{}3085\,\text{cm}^{-1}$ and/or $\sim{}3025\,\text{cm}^{-1}$ – not to be confused with the multiple band situation for aromatics (see Diagnostic Step 6).

Are there single or multiple bands between 1000 and $880\,\text{cm}^{-1}$ ($C{-}H$ out-of-plane bending)? If so, this, in combination with the 1650 and 3010 and/or 3040 cm^{-1} bands, can be used as an assignment of unsaturation. This is either terminal (or vinyl $-CH{=}CH_2$), with a pair of bands, normally located about $990\,\text{cm}^{-1}$ and close to $900\,\text{cm}^{-1}$, or trans unsaturation ($CH{=}CH$), with a band centered around 965–960 cm^{-1}. A single band around $890\,\text{cm}^{-1}$, in conjunction with the other unsaturation absorptions, can indicate a vinylidene (or pendant, $C{=}CH_2$) type of olefinic double bond.

Note that a *cis* configuration ($CH{=}CH$) is sometimes hard to characterize, because the normally characteristic $C{-}H$ out-of-plane bending is broad, with only a moderate absorption, and occurs in a region (around $700\,\text{cm}^{-1}$) where it can overlap with absorptions from other structural components, such as long-chain aliphatics, aromatics, and halogen compounds.

5.1.6 Diagnostic Step 6: Testing for Aromatics – Well-defined Absorptions in the Region 1615–1495 cm^{-1}

One, but typically two, sets of bands in the region, with one set around $1600\,\text{cm}^{-1}$ and the other around $1500\,\text{cm}^{-1}$, are consistent with an aromatic compound. Sometimes the absorptions occur as single bands, at other times one or more of the band sets may appear split, as an asymmetric doublet. This assignment is usually confirmed by the presence of other bands in the spectrum.

Are there a series of weak-to-moderate absorptions in the region 3150–3000 cm^{-1}, which can be assigned to aromatic $C{-}H$ stretching? These usually support the presence of the 1600/1500 cm^{-1} aromatic ring bands (see Diagnostic Step 2).

For simple aromatic compounds, a series of weak absorptions may be observed between 2000 and 1700 cm^{-1}. These are multiple combination bands that are noticeably weak, and are typically not to be confused with an isolated weak carbonyl absorption.

The C−H bending vibrations can also be used to support the presence of an aromatic structure. If there are medium-to-strong absorptions, sometimes more than one, between 850 and 670 cm^{-1}, these can be assigned to C−H out-of-plane bending on an aromatic ring. These support the assignment of the 1600/1500 cm^{-1} bands, and the locations of the bands are often indicative of the nature of the substitution of the aromatic ring. For simple structures, it is possible to differentiate mono-, di- (ortho, meta and para), and certain poly-substitutions. Note that a single, strong band may support simple ortho (around 750 cm^{-1}) or para (around 830 cm^{-1}) substitution.

Many organic compounds have multiple band structures in the region 1150–950 cm^{-1}. The in-plane C−H bending vibrations of aromatic compounds typically occur in this region, and can exist as complex band structures (multiple, well-defined bands). They tend not to be diagnostic for many compounds because of conflict and overlap with other functional group absorptions, including some skeletal (backbone) vibrations. However, they are clearly observable in simple hydrocarbons as weak-to-moderate absorptions, and in halogen-substituted aromatic compounds (such as chlorobenzenes) as characteristic strong absorptions.

5.1.7 Diagnostic Step 7: Testing for Multiple Bonding (Often with a Bond Order of 2 or Higher) – Absorption in the Region 2300–1990 cm^{-1}

Multiply bonded nitrogen compounds and cumulated multiple bond compounds, such as cyanides (nitriles), cyanates, isocyanates, thiocyanates, and diazo compounds, exhibit characteristic absorptions in the region 2300–1990 cm^{-1}. Cyanide absorptions vary from weak to moderate to strong, depending on the nature of other substituents in the molecule. Conjugation, including substitution on an aromatic ring, modifies the intensity of this absorption.

If the absorption band is extremely strong, the group is more likely to be a three-center functionality, such as a cyanate, an isocyanate, or a thiocyanate.

Acetylenes and alkyne substituents also exhibit a weak-to-moderate absorption within the same spectral region. If the acetylenic function is internal (medial), then the absorption can be extremely weak. However, a terminal alkyne group (C≡C) band may have moderate intensity, and this is supported by a characteristic C−H stretching absorption around 3310 cm^{-1}. A relatively low-frequency C−H bending vibration around 630 cm^{-1} also confirms the terminal alkyne vibration.

Metal carbonyls have unique bonding, where the bond order between the carbon and oxygen is between two and three, and where the additional electrons are provided by dπ back-bonding from the accompanying transition metal atom. The multiply bonded CO group provides an extremely intense absorption band close to 2000 cm^{-1} (typically between 2100 and 1900 cm^{-1}), the actual position of the band(s) and the complexity of the bands being dependent on the structure of the compound.

Note that an isolated weak-to-moderate intensity absorption above the specified region, and typically between 2700 and 2400 cm^{-1}, is not normally associated with a multiply bonded compound. These absorptions are usually from hydride vibrations, such as from silanes (Si−H), thiols and sulfides (S−H), phosphines (P−H), arsines (As−H), boranes (B−H), etc. Knowledge of the existence of the accompanying heteroatom helps in the assignment of the X−H bonds in these compounds.

This concludes the summary data for a first-pass assessment of an infrared spectrum, based on the most common and characteristic group frequencies. The technique is not foolproof, but for many simple compounds, if one systematically applies the diagnostic tests on the spectrum from a sample, as presented above, it is possible to gain some understanding of the chemical functionality. It is always hoped that more information can be gained from the sample, either by first-hand knowledge or by asking questions, or by performing additional tests. Once a basic interpretation is accomplished, and the sample is broadly characterized, it is recommended that reference spectra are used to try to obtain a more exact match to the sample. Always bear in mind that the sample could be a mixture, such as a commercially formulated/compounded material. In such cases, an exact match may not be possible, unless the reference spectrum exists for the formulation.

ABBREVIATIONS AND ACRONYMS

ATR   Attenuated Total Reflectance

RELATED ARTICLES

Infrared Spectroscopy **(Volume 12)**
Quantitative Analysis, Infrared • Theory of Infrared Spectroscopy

REFERENCES

1. H.A. Szymanski, R.E. Erickson, *Infrared Band Handbook*, Plenum Press, New York, 2 Volumes, 1970.
2. P. Gans, *Vibrating Molecules: an Introduction to the Interpretation of Infrared and Raman Spectra*, Chapman & Hall, London, 1975.
3. N.B. Colthrup, L.H. Daly, S.E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, San Diego, CA, 1–73, 1990.
4. J.M. Hollas, *Modern Spectroscopy*, 3rd edition, John Wiley & Sons, New York, 1996.
5. J.P. Coates, 'The Interpretation of Infrared Spectra: Published Reference Sources', *Appl. Spectrosc. Rev.*, **31**(1–2), 179–192 (1996).
6. L.J. Bellamy, *Infrared Spectra of Complex Molecules*, Chapman & Hall, New York, Vol. 1, 1975.
7. L.J. Bellamy, *Advances in Infrared Group Frequencies, Infrared Spectra of Complex Molecules*, Chapman & Hall, New York, Vol. 2, 1980.
8. D. Steele, *Interpretation of Vibrational Spectra*, Chapman & Hall, London, 1971.
9. N.B. Colthrup, L.H. Daly, S.E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, San Diego, CA, 1990.
10. G. Socrates, *Infrared Characteristic Group Frequencies*, John Wiley & Sons, New York, 1994.
11. D. Lin-Vien, N.B. Colthup, W.G. Fateley, J.G. Grasselli, *Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, San Diego, CA, 1991.
12. B. Smith, *Infrared Spectral Interpretation, a Systematic Approach*, CRC Press, Boca Raton, FL, 1999.
13. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Parts A and B*, John Wiley & Sons, New York, 1997.
14. R.A. Nyquist, C.L. Putzig, M.A. Leugers, *Handbook of Infrared and Raman Spectra of Inorganic Compounds and Organic Salts*, Academic Press, San Diego, CA, 1997.
15. J. Haslam, H.A. Willis, D.C. Squirrel, *Identification and Analysis of Plastics*, John Wiley & Sons, New York, 1979; originally published by Iliffe, London, 1972.
16. D.O. Hummel, F.K. Scholl, *Atlas of Polymer and Plastics Analysis*, Verlag Chemie, Weinheim, Vol. 1–3, 1980–81.
17. J.L. Koenig, *Spectroscopy of Polymers*, American Chemical Society, Washington, DC, 1992.
18. J.P. Coates, 'Questions and Answers: What to Do When the Sample Arrives, Part II', *Spectroscopy*, **11**(5), 24–32 (1996).
19. J.P. Coates, 'Into the Unknown: the First in the Series', *Spectroscopy*, **11**(5), 32–39 (1996).
20. J.P. Coates, 'Once More into the Unknown', *Spectroscopy*, **11**(6), 14–23 (1996).
21. J.P. Coates, 'A Review of Sampling Methods for Infrared Spectroscopy', in *Applied Spectroscopy: a Compact Reference for Practitioners*, eds. J. Workman, A.W. Sprinsteen, Academic Press, New York, 49–91, 1998.
22. P.B. Coleman (ed.), *Practical Sampling Techniques for Infrared Analysis*, CRC Press, Boca Raton, FL, 1993.
23. G. Dent, J.M. Chalmers, *Industrial Analysis with Vibrational Spectroscopy*, Royal Society of Chemistry, Cambridge, 1997.