INFRARED SPECTROSCOPY: FUNDAMENTALS AND APPLICATIONS

Infrared Spectroscopy: Fundamentals and Applications B. Stuart
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Series Preface

There has been a rapid expansion in the provision of further education in recent years, which has brought with it the need to provide more flexible methods of teaching in order to satisfy the requirements of an increasingly more diverse type of student. In this respect, the *open learning* approach has proved to be a valuable and effective teaching method, in particular for those students who for a variety of reasons cannot pursue full-time traditional courses. As a result, John Wiley & Sons, Ltd first published the Analytical Chemistry by Open Learning (ACOL) series of textbooks in the late 1980s. This series, which covers all of the major analytical techniques, rapidly established itself as a valuable teaching resource, providing a convenient and flexible means of studying for those people who, on account of their individual circumstances, were not able to take advantage of more conventional methods of education in this particular subject area.

Following upon the success of the ACOL series, which by its very name is predominately concerned with Analytical *Chemistry*, the *Analytical Techniques in the Sciences* (AnTS) series of open learning texts has been introduced with the aim of providing a broader coverage of the many areas of science in which analytical techniques and methods are now increasingly applied. With this in mind, the AnTS series of texts seeks to provide a range of books which will cover not only the actual techniques themselves, but *also* those scientific disciplines which have a necessary requirement for analytical characterization methods.

Analytical instrumentation continues to increase in sophistication, and as a consequence, the range of materials that can now be almost routinely analysed has increased accordingly. Books in this series which are concerned with the *techniques* themselves will reflect such advances in analytical instrumentation, while at the same time providing full and detailed discussions of the fundamental concepts and theories of the particular analytical method being considered. Such books will cover a variety of techniques, including general instrumental analysis,

spectroscopy, chromatography, electrophoresis, tandem techniques, electroanalytical methods, X-ray analysis and other significant topics. In addition, books in the series will include the *application* of analytical techniques in areas such as environmental science, the life sciences, clinical analysis, food science, forensic analysis, pharmaceutical science, conservation and archaeology, polymer science and general solid-state materials science.

Written by experts in their own particular fields, the books are presented in an easy-to-read, user-friendly style, with each chapter including both learning objectives and summaries of the subject matter being covered. The progress of the reader can be assessed by the use of frequent self-assessment questions (SAQs) and discussion questions (DQs), along with their corresponding reinforcing or remedial responses, which appear regularly throughout the texts. The books are thus eminently suitable both for self-study applications and for forming the basis of industrial company in-house training schemes. Each text also contains a large amount of supplementary material, including bibliographies, lists of acronyms and abbreviations, and tables of SI Units and important physical constants, plus, where appropriate, glossaries and references to literature sources.

It is therefore hoped that this present series of textbooks will prove to be a useful and valuable source of teaching material, both for individual students and for teachers of science courses.

Dave Ando
Dartford, UK

Preface

Infrared spectroscopy is one of the most important and widely used analytical techniques available to scientists working in a whole range of fields. There are a number of texts on the subject available, ranging from instrumentation to specific applications. This present book aims to provide an introduction to those needing to use infrared spectroscopy for the first time, by explaining the fundamental aspects of the technique, how to obtain a spectrum and how to analyse infrared data obtained for a wide number of materials.

This text is not intended to be comprehensive, as infrared spectroscopy is extensively used. However, the information provided here may be used as a starting point for more detailed investigations. The book is laid out with introductory chapters covering the background theory of infrared spectroscopy, instrumentation and sampling techniques. Scientists may require qualitative and/or quantitative analysis of infrared data and therefore a chapter is devoted to the approaches commonly used to extract such information.

Infrared spectroscopy is a versatile experimental technique. It can be used to obtain important information about everything from delicate biological samples to tough minerals. In this book, the main areas that are studied using infrared spectroscopy are examined in a series of chapters, namely organic molecules, inorganic molecules, polymers, and biological, industrial and environmental applications. Each chapter provides examples of commonly encountered molecular structures in each field and how to approach the analysis of such structures. Suitable questions and problems are included in each chapter to assist in the analysis of the relevant infrared spectra.

I very much hope that those learning about and utilizing infrared spectroscopy will find this text a useful and valuable introduction to this major analytical technique.

Barbara Stuart
University of Technology, Sydney, Australia

Acronyms, Abbreviations and Symbols

ANN	artificial neural network
ATR	attenuated total reflectance
CLS	classical least-squares
D_2O	deuterium oxide
DAC	diamond anvil cell
DNA	deoxyribonucleic acid
DOP	dioctyl phthalate
DRIFT	diffuse reflectance infrared technique
DTGS	deuterium triglycine sulfate
EGA	evolved gas analysis
en	ethylenediamine
FFT	fast Fourier-transform
FPA	focal plane array
FTIR	Fourier-transform infrared (spectroscopy)
GC–IR	gas chromatography–infrared (spectroscopy)
GC–MS	gas chromatography–mass spectrometry
HDPE	high-density polyethylene
ILS	inverse least-squares
KRS-5	thallium-iodide
LC	liquid chromatography
LDA	linear discriminant analysis
LDPE	low-density polyethylene
MBP	myelin basic protein
MCT	mercury cadmium telluride
MIR	multiple internal reflectance

MMA	methyl methacrylate
NMR	nuclear magnetic resonance (spectroscopy)
PAS	photoacoustic spectroscopy
PCA	principal component analysis
PE	polyethylene
PEO	poly(ethylene oxide)
PET	poly(ethylene terephthalate)
PLS	partial least-squares
PMMA	poly(methyl methacrylate)
PP	polypropylene
PTFE	polytetrafluoroethylene
PU	polyurethane
PVC	poly(vinyl chloride)
PVIE	poly(vinyl isobutylether)
PVPh	poly(vinyl phenol)
RNA	ribonucleic acid
SFC	supercritical fluid chromatography
SNR	signal-to-noise ratio
TFE	trifluoroethanol
TGA	thermogravimetric analysis
TGA–IR	thermogravimetric analysis–infrared (spectroscopy)

A	absorbance
$A_{\|\|}$	absorbance parallel to chain axis
$A_{\perp}$	absorbance perpendicular to chain axis
B	magnetic vector (magnitude)
$B(\bar{\nu})$	spectral power density
c	speed of light; concentration
d_{p}	penetration depth
D	optical path difference
E	energy; electric vector (magnitude)
h	Planck constant
k	force constant; molar absorption coefficient
I	transmitted light
I_0	incident light
$I(\delta)$	intensity at detector
l	pathlength
L	cell pathlength
n	number of peak-to-peak fringes; refractive index; number of moles
P	pressure
R	reflectance; universal gas constant
T	transmittance; temperature

V	volume
δ	pathlength
ε	molar absorptivity
θ	angle of incident radiation
λ	wavelength
μ	reduced mass
ν	frequency
$\bar{\nu}$	wavenumber

About the Author

Barbara Stuart, B.Sc. (Sydney), M.Sc. (Sydney), Ph.D. (London), D.I.C., MRACI, MRSC, CChem

After graduating with a B.Sc. degree from the University of Sydney in Australia, Barbara Stuart then worked as a tutor at this university. She also carried out research in the field of biophysical chemistry in the Department of Physical Chemistry and graduated with an M.Sc. in 1990. The author then moved to the UK to carry out doctoral studies in polymer engineering within the Department of Chemical Engineering and Chemical Technology at Imperial College (University of London). After obtaining her Ph.D. in 1993, she took up a position as a Lecturer in Physical Chemistry at the University of Greenwich in South East London. Barbara returned to Australia in 1995, joining the staff at the University of Technology, Sydney, where she is currently a Senior Lecturer in the Department of Chemistry, Materials and Forensic Science. She is presently conducting research in the fields of polymer spectroscopy, materials conservation and forensic science. Barbara is the author of three other books published by John Wiley and Sons, Ltd, namely *Modern Infrared Spectroscopy* and *Biological Applications of Infrared Spectroscopy*, both in the ACOL series of open learning texts, and *Polymer Analysis* in this current AnTS series of texts.

Chapter 1
Introduction

Learning Objectives

- To understand the origin of electromagnetic radiation.
- To determine the frequency, wavelength, wavenumber and energy change associated with an infrared transition.
- To appreciate the factors governing the intensity of bands in an infrared spectrum.
- To predict the number of fundamental modes of vibration of a molecule.
- To understand the influences of force constants and reduced masses on the frequency of band vibrations.
- To appreciate the different possible modes of vibration.
- To recognize the factors that complicate the interpretation of infrared spectra.

Infrared spectroscopy is certainly one of the most important analytical techniques available to today's scientists. One of the great advantages of infrared spectroscopy is that virtually any sample in virtually any state may be studied. Liquids, solutions, pastes, powders, films, fibres, gases and surfaces can all be examined with a judicious choice of sampling technique. As a consequence of the improved instrumentation, a variety of new sensitive techniques have now been developed in order to examine formerly intractable samples.

Infrared spectrometers have been commercially available since the 1940s. At that time, the instruments relied on prisms to act as dispersive elements,

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but by the mid 1950s, diffraction gratings had been introduced into dispersive machines. The most significant advances in infrared spectroscopy, however, have come about as a result of the introduction of Fourier-transform spectrometers. This type of instrument employs an interferometer and exploits the well-established mathematical process of Fourier-transformation. Fourier-transform infrared (FTIR) spectroscopy has dramatically improved the quality of infrared spectra and minimized the time required to obtain data. In addition, with constant improvements to computers, infrared spectroscopy has made further great strides.

Infrared spectroscopy is a technique based on the vibrations of the atoms of a molecule. An infrared spectrum is commonly obtained by passing infrared radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular energy. The energy at which any peak in an absorption spectrum appears corresponds to the frequency of a vibration of a part of a sample molecule. In this introductory chapter, the basic ideas and definitions associated with infrared spectroscopy will be described. The vibrations of molecules will be looked at here, as these are crucial to the interpretation of infrared spectra.

Once this chapter has been completed, some idea about the information to be gained from infrared spectroscopy should have been gained. The following chapter will aid in an understanding of how an infrared spectrometer produces a spectrum. After working through that chapter, it should be possible to record a spectrum and in order to do this a decision on an appropriate sampling technique needs to be made. The sampling procedure depends very much on the type of sample to be examined, for instance, whether it is a solid, liquid or gas. Chapter 2 also outlines the various sampling techniques that are commonly available. Once the spectrum has been recorded, the information it can provide needs to be extracted. Chapter 3, on spectrum interpretation, will assist in the understanding of the information to be gained from an infrared spectrum. As infrared spectroscopy is now used in such a wide variety of scientific fields, some of the many applications of the technique are examined in Chapters 4 to 8. These chapters should provide guidance as to how to approach a particular analytical problem in a specific field. The applications have been divided into separate chapters on organic and inorganic molecules, polymers, biological applications and industrial applications. This book is, of course, not meant to provide a comprehensive review of the use of infrared spectroscopy in each of these fields. However, an overview of the approaches taken in these areas is provided, along with appropriate references to the literature available in each of these disciplines.

1.1 Electromagnetic Radiation

The visible part of the electromagnetic spectrum is, by definition, radiation visible to the human eye. Other detection systems reveal radiation beyond the visible regions of the spectrum and these are classified as radiowave, microwave,

infrared, ultraviolet, X-ray and γ-ray. These regions are illustrated in Figure 1.1, together with the processes involved in the interaction of the radiation of these regions with matter. The electromagnetic spectrum and the varied interactions between these radiations and many forms of matter can be considered in terms of either classical or quantum theories.

The nature of the various radiations shown in Figure 1.1 have been interpreted by Maxwell's classical theory of electro- and magneto-dynamics – hence, the term *electromagnetic radiation*. According to this theory, radiation is considered as two mutually perpendicular electric and magnetic fields, oscillating in single planes at right angles to each other. These fields are in phase and are being propagated as a sine wave, as shown in Figure 1.2. The magnitudes of the electric and magnetic vectors are represented by E and B, respectively.

A significant discovery made about electromagnetic radiation was that the velocity of propagation in a vacuum was constant for all regions of the spectrum. This is known as the velocity of light, c, and has the value $2.997\,925 \times 10^8$ m s^{-1}. If one complete wave travelling a fixed distance each cycle is visualized, it may be observed that the velocity of this wave is the product of the *wavelength*, λ (the distance between adjacent peaks), and the *frequency*, ν (the number of cycles

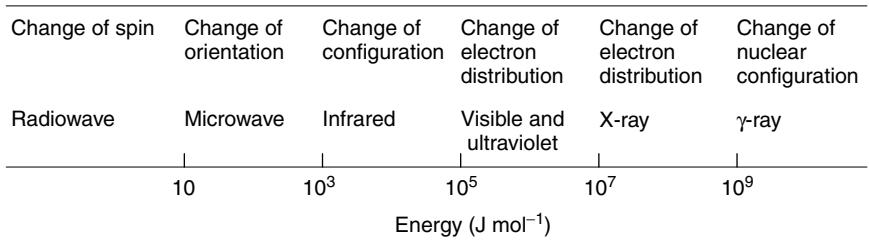

Figure 1.1 Regions of the electromagnetic spectrum. From Stuart, B., *Biological Applications of Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1997. © University of Greenwich, and reproduced by permission of the University of Greenwich.

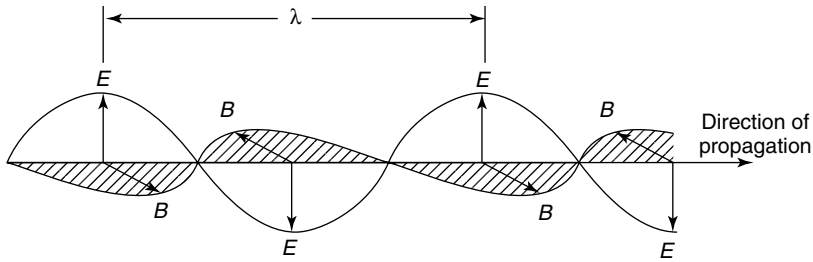

Figure 1.2 Representation of an electromagnetic wave. Reproduced from Brittain, E. F. H., George, W. O. and Wells, C. H. J., *Introduction to Molecular Spectroscopy*, Academic Press, London, Copyright (1975), with permission from Elsevier.

per second). Therefore:

$$c = \lambda\nu \tag{1.1}$$

The presentation of spectral regions may be in terms of wavelength as metres or sub-multiples of a metre. The following units are commonly encountered in spectroscopy:

$$1\ \text{Å} = 10^{-10}\ \text{m} \qquad 1\ \text{nm} = 10^{-9}\ \text{m} \qquad 1\ \mu\text{m} = 10^{-6}\ \text{m}$$

Another unit which is widely used in infrared spectroscopy is the *wavenumber*, $\overline{\nu}$, in cm^{-1}. This is the number of waves in a length of one centimetre and is given by the following relationship:

$$\overline{\nu} = 1/\lambda = \nu/c \tag{1.2}$$

This unit has the advantage of being linear with energy.

During the 19th Century, a number of experimental observations were made which were not consistent with the classical view that matter could interact with energy in a continuous form. Work by Einstein, Planck and Bohr indicated that in many ways electromagnetic radiation could be regarded as a stream of particles (or quanta) for which the energy, E, is given by the Bohr equation, as follows:

$$E = h\nu \tag{1.3}$$

where h is the Planck constant ($h = 6.626 \times 10^{-34}$ J s) and ν is equivalent to the classical frequency.

Processes of change, including those of vibration and rotation associated with infrared spectroscopy, can be represented in terms of quantized discrete energy levels E_0, E_1, E_2, etc., as shown in Figure 1.3. Each atom or molecule in a system must exist in one or other of these levels. In a large assembly of molecules, there will be a distribution of all atoms or molecules among these various energy levels. The latter are a function of an integer (the *quantum number*) and a parameter associated with the particular atomic or molecular process associated with that state. Whenever a molecule interacts with radiation, a quantum of energy (or

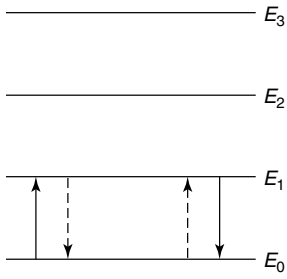

Figure 1.3 Illustration of quantized discrete energy levels.

photon) is either emitted or absorbed. In each case, the energy of the quantum of radiation must exactly fit the energy gap $E_1 - E_0$ or $E_2 - E_1$, etc. The energy of the quantum is related to the frequency by the following:

$$\Delta E = h\nu \tag{1.4}$$

Hence, the frequency of emission or absorption of radiation for a transition between the energy states E_0 and E_1 is given by:

$$\nu = (E_1 - E_0)/h \tag{1.5}$$

Associated with the uptake of energy of quantized absorption is some deactivation mechanism whereby the atom or molecule returns to its original state. Associated with the loss of energy by emission of a quantum of energy or photon is some prior excitation mechanism. Both of these associated mechanisms are represented by the dotted lines in Figure 1.3.

SAQ 1.1

Caffeine molecules absorb infrared radiation at 1656 cm^{-1}. Calculate the following:

(i) wavelength of this radiation;

(ii) frequency of this radiation;

(iii) energy change associated with this absorption.

1.2 Infrared Absorptions

For a molecule to show infrared absorptions it must possess a specific feature, i.e. an electric dipole moment of the molecule must change during the vibration. This is the *selection rule* for infrared spectroscopy. Figure 1.4 illustrates an example of an 'infrared-active' molecule, a *heteronuclear* diatomic molecule. The dipole moment of such a molecule changes as the bond expands and contracts. By comparison, an example of an 'infrared-inactive' molecule is a *homonuclear* diatomic molecule because its dipole moment remains zero no matter how long the bond.

An understanding of molecular symmetry and group theory is important when initially assigning infrared bands. A detailed description of such theory is beyond the scope of this book, but symmetry and group theory are discussed in detail in other texts [1, 2]. Fortunately, it is not necessary to work from first principles each time a new infrared spectrum is obtained.

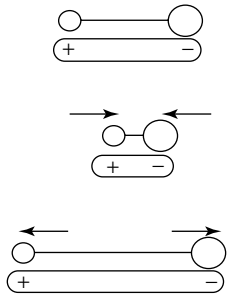

Figure 1.4 Change in the dipole moment of a heteronuclear diatomic molecule.

Infrared absorptions are not infinitely narrow and there are several factors that contribute to the broadening. For gases, the Doppler effect, in which radiation is shifted in frequency when the radiation source is moving towards or away from the observer, is a factor. There is also the broadening of bands due to the collisions between molecules. Another source of line broadening is the finite lifetime of the states involved in the transition. From quantum mechanics, when the Schrödinger equation is solved for a system which is changing with time, the energy states of the system do not have precisely defined energies and this leads to lifetime broadening. There is a relationship between the lifetime of an excited state and the bandwidth of the absorption band associated with the transition to the excited state, and this is a consequence of the *Heisenberg Uncertainty Principle*. This relationship demonstrates that the shorter the lifetime of a state, then the less well defined is its energy.

1.3 Normal Modes of Vibration

The interactions of infrared radiation with matter may be understood in terms of changes in molecular dipoles associated with vibrations and rotations. In order to begin with a basic model, a molecule can be looked upon as a system of masses joined by bonds with spring-like properties. Taking first the simple case of diatomic molecules, such molecules have three degrees of translational freedom and two degrees of rotational freedom. The atoms in the molecules can also move relative to one other, that is, bond lengths can vary or one atom can move out of its present plane. This is a description of stretching and bending movements that are collectively referred to as *vibrations*. For a diatomic molecule, only one vibration that corresponds to the stretching and compression of the bond is possible. This accounts for one degree of vibrational freedom.

Polyatomic molecules containing many (N) atoms will have $3N$ degrees of freedom. Looking first at the case of molecules containing three atoms, two groups of triatomic molecules may be distinguished, i.e. linear and non-linear. Two simple examples of linear and non-linear triatomics are represented by CO_2

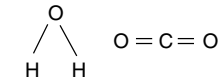

Figure 1.5 Carbon dioxide and water molecules.

Table 1.1 Degrees of freedom for polyatomic molecules. From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich

Type of degrees of freedom	Linear	Non-linear
Translational	3	3
Rotational	2	3
Vibrational	$3N - 5$	$3N - 6$
Total	$3N$	$3N$

and H_2O, respectively (illustrated in Figure 1.5). Both CO_2 and H_2O have three degrees of translational freedom. Water has three degrees of rotational freedom, but the linear molecule carbon dioxide has only two since no detectable energy is involved in rotation around the O=C=O axis. Subtracting these from $3N$, there are $3N-5$ degrees of freedom for CO_2 (or any linear molecule) and $3N-6$ for water (or any non-linear molecule). N in both examples is three, and so CO_2 has four vibrational modes and water has three. The degrees of freedom for polyatomic molecules are summarized in Table 1.1.

SAQ 1.2

How many vibrational degrees of freedom does a chloroform ($CHCl_3$) molecule possess?

Whereas a diatomic molecule has only one mode of vibration which corresponds to a stretching motion, a non-linear B–A–B type triatomic molecule has three modes, two of which correspond to stretching motions, with the remainder corresponding to a bending motion. A linear type triatomic has four modes, two of which have the same frequency, and are said to be *degenerate*.

Two other concepts are also used to explain the frequency of vibrational modes. These are the stiffness of the bond and the masses of the atoms at each end of the bond. The stiffness of the bond can be characterized by a proportionality constant termed the *force constant*, k (derived from Hooke's law). The *reduced mass*, μ, provides a useful way of simplifying our calculations by combining the individual atomic masses, and may be expressed as follows:

$$(1/\mu) = (1/m_1) + (1/m_2) \tag{1.6}$$

where m_1 and m_2 are the masses of the atoms at the ends of the bond. A practical alternative way of expressing the reduced mass is:

$$\mu = m_1 m_2/(m_1 + m_2) \tag{1.7}$$

The equation relating the force constant, the reduced mass and the frequency of absorption is:

$$\nu = (1/2\pi)\sqrt{(k/\mu)} \tag{1.8}$$

This equation may be modified so that direct use of the wavenumber values for bond vibrational frequencies can be made, namely:

$$\overline{\nu} = (1/2\pi c)\sqrt{(k/\mu)} \tag{1.9}$$

where c is the speed of light.

A molecule can only absorb radiation when the incoming infrared radiation is of the same frequency as one of the fundamental modes of vibration of the molecule. This means that the vibrational motion of a small part of the molecule is increased while the rest of the molecule is left unaffected.

SAQ 1.3

Given that the C–H stretching vibration for chloroform occurs at 3000 cm^{-1}, calculate the C–D stretching frequency for deuterochloroform. The relevant atomic masses are $^1H = 1.674 \times 10^{-27}$ kg, $^2H = 3.345 \times 10^{-27}$ kg and $^{12}C = 1.993 \times 10^{-27}$ kg.

Vibrations can involve either a change in bond length (*stretching*) or bond angle (*bending*) (Figure 1.6). Some bonds can stretch in-phase (*symmetrical* stretching) or out-of-phase (*asymmetric* stretching), as shown in Figure 1.7. If a molecule has different terminal atoms such as HCN, ClCN or ONCl, then the two stretching modes are no longer symmetric and asymmetric vibrations of similar bonds, but will have varying proportions of the stretching motion of each group. In other words, the amount of *coupling* will vary.

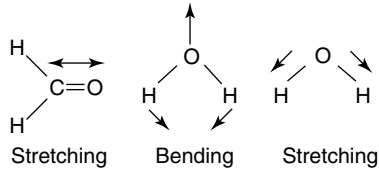

Figure 1.6 Stretching and bending vibrations.

Figure 1.7 Symmetric and asymmetric stretching vibrations.

Bending vibrations also contribute to infrared spectra and these are summarized in Figure 1.8. It is best to consider the molecule being cut by a plane through the hydrogen atoms and the carbon atom. The hydrogens can move in the same direction or in opposite directions in this plane, here the plane of the page. For more complex molecules, the analysis becomes simpler since hydrogen atoms may be considered in isolation because they are usually attached to more massive, and therefore, more rigid parts of the molecule. This results in *in-plane* and *out-of-plane* bending vibrations, as illustrated in Figure 1.9.

As already mentioned, for a vibration to give rise to the absorption of infrared radiation, it must cause a change in the dipole moment of the molecule. The larger this change, then the more intense will be the absorption band. Because of the difference in electronegativity between carbon and oxygen, the carbonyl group is permanently polarized, as shown in Figure 1.10. Stretching this bond will increase the dipole moment and, hence, C=O stretching is an intense absorption. In CO_2, two different stretching vibrations are possible: (a) symmetric and (b) asymmetric (Figure 1.11). In practice, this 'black and white' situation does not prevail. The change in dipole may be very small and, hence, lead to a very weak absorption.

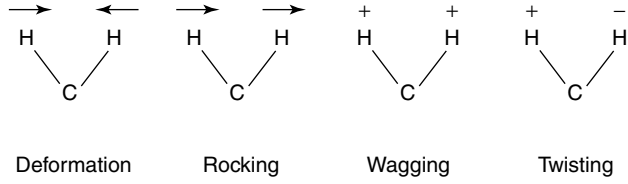

Figure 1.8 Different types of bending vibrations.

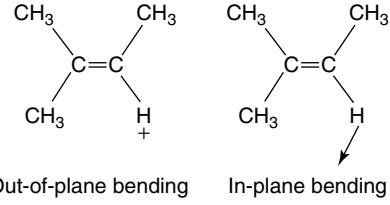

Figure 1.9 Out-of-plane and in-plane bending vibrations.

Figure 1.10 Dipole moment in a carbonyl group.

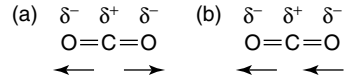

Figure 1.11 Stretching vibrations of carbon dioxide.

DQ 1.1

Which one of the vibrations shown in Figure 1.11 is 'infrared-inactive'?

Answer

A dipole moment is a vector sum. CO_2 in the ground state, therefore, has no dipole moment. If the two C=O bonds are stretched symmetrically, there is still no net dipole and so there is no infrared activity. However, in the asymmetric stretch, the two C=O bonds are of different length and, hence, the molecule has a dipole. Therefore, the vibration shown in Figure 1.11(b) is 'infrared-active'.

SAQ 1.4

Consider the symmetrical bending vibration of CO_2, as shown in Figure 1.12. Will this vibration be 'active' in the infrared?

Figure 1.12 Symmetric bending vibration of carbon dioxide (cf. SAQ 1.4).

Symmetrical molecules will have fewer 'infrared-active' vibrations than asymmetrical molecules. This leads to the conclusion that symmetric vibrations will generally be weaker than asymmetric vibrations, since the former will not lead to a change in dipole moment. It follows that the bending or stretching of bonds involving atoms in widely separated groups of the periodic table will lead to intense bands. Vibrations of bonds such as C–C or N=N will give weak bands. This again is because of the small change in dipole moment associated with their vibrations.

There will be many different vibrations for even fairly simple molecules. The complexity of an infrared spectrum arises from the coupling of vibrations over a large part of or over the complete molecule. Such vibrations are called *skeletal* vibrations. Bands associated with skeletal vibrations are likely to conform to a

pattern or *fingerprint* of the molecule as a whole, rather than a specific group within the molecule.

1.4 Complicating Factors

There are a number of factors that may complicate the interpretation of infrared spectra. These factors should be considered when studying spectra as they can result in important changes to the spectra and may result in the misinterpretation of bands.

1.4.1 Overtone and Combination Bands

The sound we hear is a mixture of harmonics, that is, a fundamental frequency mixed with multiples of that frequency. *Overtone bands* in an infrared spectrum are analogous and are multiples of the fundamental absorption frequency. The energy levels for overtones of infrared modes are illustrated in Figure 1.13. The energy required for the first overtone is twice the fundamental, assuming evenly spaced energy levels. Since the energy is proportional to the frequency absorbed and this is proportional to the wavenumber, the first overtone will appear in the spectrum at twice the wavenumber of the fundamental.

Combination bands arise when two fundamental bands absorbing at $\overline{\nu}_1$ and $\overline{\nu}_2$ absorb energy simultaneously. The resulting band will appear at $(\overline{\nu}_1 + \overline{\nu}_2)$ wavenumbers.

SAQ 1.5

A molecule has strong fundamental bands at the following wavenumbers:

C–H bending at 730 cm^{-1}

C–C stretching at 1400 cm^{-1}

C–H stretching at 2950 cm^{-1}

Determine the wavenumbers of the possible combination bands and the first overtones.

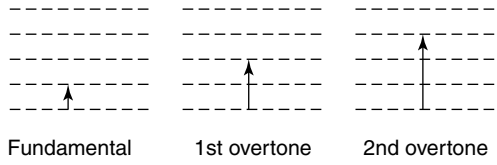

Figure 1.13 Energy levels for fundamental and overtone infrared bands.

1.4.2 Fermi Resonance

The Fermi resonance effect usually leads to two bands appearing close together when only one is expected. When an overtone or a combination band has the same frequency as, or a similar frequency to, a fundamental, two bands appear, split either side of the expected value and are of about equal intensity. The effect is greatest when the frequencies match, but it is also present when there is a mismatch of a few tens of wavenumbers. The two bands are referred to as a *Fermi doublet*.

1.4.3 Coupling

Vibrations in the skeletons of molecules become coupled, as mentioned in Section 1.4. Such vibrations are not restricted to one or two bonds, but may involve a large part of the carbon backbone and oxygen or nitrogen atoms if present. The energy levels mix, hence resulting in the same number of vibrational modes, but at different frequencies, and bands can no longer be assigned to one bond. This is very common and occurs when adjacent bonds have similar frequencies. Coupling commonly occurs between C–C stretching, C–O stretching, C–N stretching, C–H rocking and C–H wagging motions. A further requirement is that to be strongly coupled, the motions must be in the same part of the molecule.

1.4.4 Vibration–Rotation Bands

When the infrared spectra of gaseous heteronuclear molecules are analysed at high resolution, a series of closely spaced components are observed. This type of structure is due to the excitation of rotational motion during a vibrational transition and is referred to as an vibration–rotation spectrum [1]. The absorptions fall into groups called branches and are labelled P, Q and R according to the change in the rotational quantum number associated with the transition. The separation of the lines appearing in a vibration–rotation spectrum may be exploited to determine the bond length of the molecule being examined.

Summary

The ideas fundamental to an understanding of infrared spectroscopy were introduced in this chapter. The electromagnetic spectrum was considered in terms of various atomic and molecular processes and classical and quantum ideas were introduced. The vibrations of molecules and how they produce infrared spectra were then examined. The various factors that are responsible for the position and intensity of infrared modes were described. Factors such as combination and overtone bands, Fermi resonance, coupling and vibration–rotation bands can lead to changes in infrared spectra. An appreciation of these issues is important when

examining spectra and these factors were outlined in this chapter. For further reference, there is a range of books and book chapters available which provide an overview of the theory behind infrared spectroscopy [3–7].

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Chapter 2
Experimental Methods

Learning Objectives

- To understand how an infrared spectrum is obtained from a Fourier-transform instrument.
- To recognize the different methods of sample preparation and sample handling techniques which are used for preparing samples in infrared spectroscopy.
- To recognize poor quality spectra and diagnose their causes.
- To understand the origins of reflectance techniques.
- To understand the origins of infrared microsampling techniques.
- To understand that spectral information may be obtained from combination infrared spectroscopy techniques.
- To select appropriate sample preparation methods for different types of samples.

2.1 Introduction

Traditionally, dispersive instruments, available since the 1940s, were used to obtain infrared spectra. In recent decades, a very different method of obtaining an infrared spectrum has superceded the dispersive instrument. Fourier-transform infrared spectrometers are now predominantly used and have improved the acquisition of infrared spectra dramatically. In this present chapter, the instrumentation required to obtain an infrared spectrum will be described.

Infrared spectroscopy is a versatile experimental technique and it is relatively easy to obtain spectra from samples in solution or in the liquid, solid or gaseous

Infrared Spectroscopy: Fundamentals and Applications B. Stuart
 ISBNs: 0-470-85427-8 (HB); 0-470-85428-6 (PB)

states. In this chapter, how samples can be introduced into the instrument, the equipment required to obtain spectra and the pre-treatment of samples are examined. First, the various ways of investigating samples using the traditional transmission methods of infrared spectroscopy will be discussed. Reflectance methods, such as the attenuated total reflectance, diffuse reflectance and specular reflectance approaches, as well as photoacoustic spectroscopy, are also explained. Infrared microspectroscopy has emerged in recent years as an effective tool for examining small and/or complex samples; the techniques used are described in this chapter. Infrared spectroscopy has also been combined with other well-established analytical techniques such as chromatography and thermal analysis. Such combination techniques are introduced here.

2.2 Dispersive Infrared Spectrometers

The first dispersive infrared instruments employed prisms made of materials such as sodium chloride. The popularity of prism instruments fell away in the 1960s when the improved technology of grating construction enabled cheap, good-quality gratings to be manufactured.

The dispersive element in dispersive instruments is contained within a monochromator. Figure 2.1 shows the optical path of an infrared spectrometer which uses a grating monochromator. Dispersion occurs when energy falling on the entrance slit is collimated onto the dispersive element and the dispersed radiation is then reflected back to the exit slit, beyond which lies the detector. The dispersed spectrum is scanned across the exit slit by rotating a suitable component within the monochromator. The widths of the entrance and exit slits may be varied and programmed to compensate for any variation of the source energy with wavenumber. In the absence of a sample, the detector then receives radiation of approximately constant energy as the spectrum is scanned.

Atmospheric absorption by CO_2 and H_2O in the instrument beam has to be considered in the design of infrared instruments. Figure 2.2 shows the spectrum of such atmospheric absorptions. These contributions can be taken into account by using a double-beam arrangement in which radiation from a source is divided into two beams. These beams pass through a sample and a reference path of the sample compartment, respectively. The information from these beams is rationed to obtain the required sample spectrum.

A detector must have adequate sensitivity to the radiation arriving from the sample and monochromator over the entire spectral region required. In addition, the source must be sufficiently intense over the wavenumber range and transmittance range. Sources of infrared emission have included the Globar, which is constructed of silicon carbide. There is also the Nernst filament, which is a mixture of the oxides of zirconium, yttrium and erbium. A Nernst filament only conducts electricity at elevated temperatures. Most detectors have consisted of thermocouples of varying characteristics.

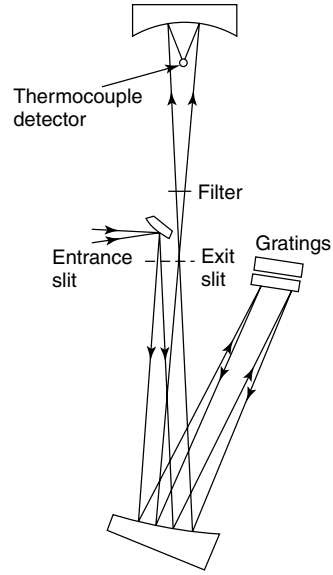

Figure 2.1 Schematic of the optical path of a double-beam infrared spectrometer with a grating monochromator. Reproduced from Brittain, E. F. H., George, W. O. and Wells, C. H. J., *Introduction to Molecular Spectroscopy*, Academic Press, London, Copyright (1975), with permission from Elsevier.

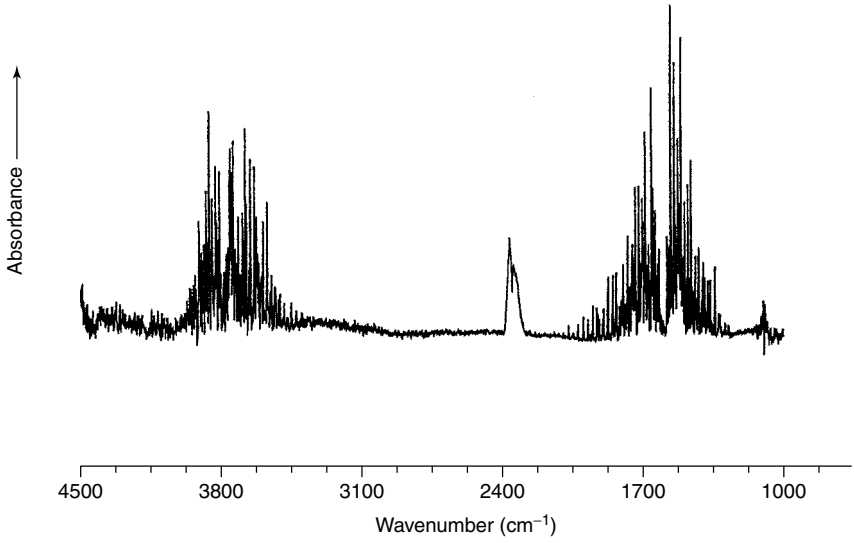

Figure 2.2 Infrared spectrum of atmospheric contributions (e.g. CO_2 and H_2O). From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

The essential problem of the dispersive spectrometer lies with its monochromator. This contains narrow slits at the entrance and exit which limit the wavenumber range of the radiation reaching the detector to one resolution width. Samples for which a very quick measurement is needed, for example, in the eluant from a chromatography column, cannot be studied with instruments of low sensitivity because they cannot scan at speed. However, these limitations may be overcome through the use of a Fourier-transform infrared spectrometer.

2.3 Fourier-Transform Infrared Spectrometers

Fourier-transform infrared (FTIR) spectroscopy [1] is based on the idea of the interference of radiation between two beams to yield an *interferogram*. The latter is a signal produced as a function of the change of pathlength between the two beams. The two domains of distance and frequency are interconvertible by the mathematical method of *Fourier-transformation*.

The basic components of an FTIR spectrometer are shown schematically in Figure 2.3. The radiation emerging from the source is passed through an interferometer to the sample before reaching a detector. Upon amplification of the signal, in which high-frequency contributions have been eliminated by a filter, the data are converted to digital form by an analog-to-digital converter and transferred to the computer for Fourier-transformation.

2.3.1 Michelson Interferometers

The most common interferometer used in FTIR spectrometry is a Michelson interferometer, which consists of two perpendicularly plane mirrors, one of which can travel in a direction perpendicular to the plane (Figure 2.4). A semi-reflecting film, the *beamsplitter*, bisects the planes of these two mirrors. The beamsplitter material has to be chosen according to the region to be examined. Materials such as germanium or iron oxide are coated onto an 'infrared-transparent' substrate such as potassium bromide or caesium iodide to produce beamsplitters for the mid- or near-infrared regions. Thin organic films, such as poly(ethylene terephthalate), are used in the far-infrared region.

If a collimated beam of monochromatic radiation of wavelength λ (cm) is passed into an ideal beamsplitter, 50% of the incident radiation will be reflected to one of the mirrors while 50% will be transmitted to the other mirror. The two beams are reflected from these mirrors, returning to the beamsplitter where they recombine and interfere. Fifty percent of the beam reflected from the fixed

Figure 2.3 Basic components of an FTIR spectrometer.

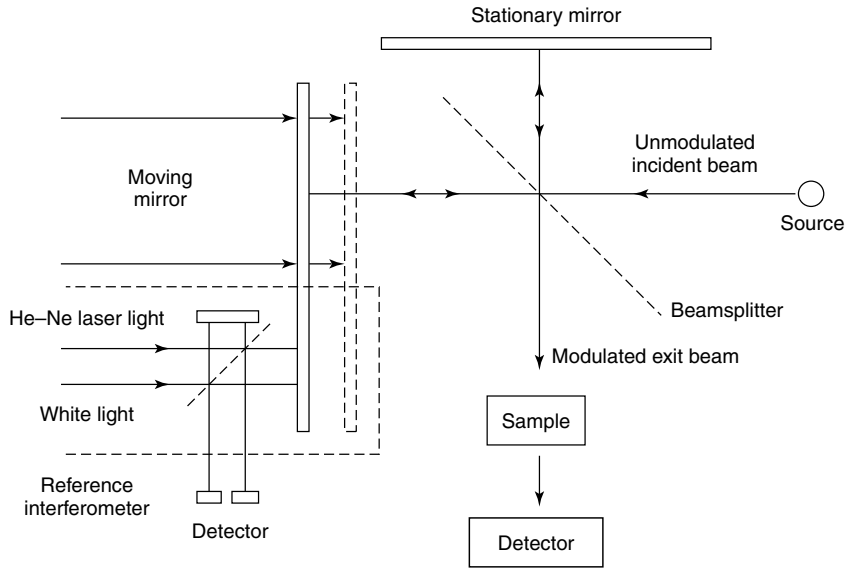

Figure 2.4 Schematic of a Michelson interferometer. From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

mirror is transmitted through the beamsplitter while 50% is reflected back in the direction of the source. The beam which emerges from the interferometer at 90° to the input beam is called the transmitted beam and this is the beam detected in FTIR spectrometry.

The moving mirror produces an optical path difference between the two arms of the interferometer. For path differences of $(n + 1/2)\lambda$, the two beams interfere destructively in the case of the transmitted beam and constructively in the case of the reflected beam. The resultant interference pattern is shown in Figure 2.5 for (a) a source of monochromatic radiation and (b) a source of polychromatic radiation (b). The former is a simple cosine function, but the latter is of a more complicated form because it contains all of the spectral information of the radiation falling on the detector.

2.3.2 Sources and Detectors

FTIR spectrometers use a Globar or Nernst source for the mid-infrared region. If the far-infrared region is to be examined, then a high-pressure mercury lamp can be used. For the near-infrared, tungsten–halogen lamps are used as sources.

There are two commonly used detectors employed for the mid-infrared region. The normal detector for routine use is a pyroelectric device incorporating deuterium tryglycine sulfate (DTGS) in a temperature-resistant alkali halide window.

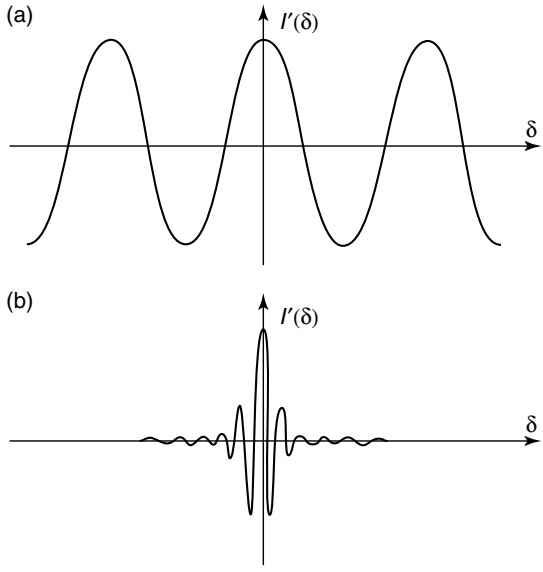

Figure 2.5 Interferograms obtained for (a) monochromatic radiation and (b) polychromatic radiation. Reproduced with permission from Barnes, A. J. and Orville-Thomas, W. J. (Eds), *Vibrational Spectroscopy – Modern Trends*, Elsevier, Amsterdam, Figure 2, p. 55 (1977).

For more sensitive work, mercury cadmium telluride (MCT) can be used, but this has to be cooled to liquid nitrogen temperatures. In the far-infrared region, germanium or indium–antimony detectors are employed, operating at liquid helium temperatures. For the near-infrared region, the detectors used are generally lead sulfide photoconductors.

2.3.3 Fourier-Transformation

The essential equations for a Fourier-transformation relating the intensity falling on the detector, $I(\delta)$, to the spectral power density at a particular wavenumber, $\bar{\nu}$, given by $B(\bar{\nu})$, are as follows:

$$I(\delta) = \int_0^{+\infty} B(\bar{\nu})\cos\,(2\pi\bar{\nu}\delta)d\bar{\nu} \tag{2.1}$$

which is one half of a cosine Fourier-transform pair, with the other being:

$$B(\bar{\nu}) = \int_{-\infty}^{+\infty} I(\delta)\cos\,(2\pi\bar{\nu}\delta)d\delta \tag{2.2}$$

These two equations are interconvertible and are known as a Fourier-transform pair. The first shows the variation in power density as a function of the difference in pathlength, which is an interference pattern. The second shows the variation in intensity as a function of wavenumber. Each can be converted into the other by the mathematical method of *Fourier-transformation*.

The essential experiment to obtain an FTIR spectrum is to produce an interferogram with and without a sample in the beam and transforming the interferograms into spectra of (a) the source with sample absorptions and (b) the source without sample absorptions. The ratio of the former and the latter corresponds to a double-beam dispersive spectrum.

The major advance toward routine use in the mid-infrared region came with a new mathematical method (or algorithm) devised for *fast Fourier-transformation* (FFT). This was combined with advances in computers which enabled these calculations to be carried out rapidly.

2.3.4 Moving Mirrors

The moving mirror is a crucial component of the interferometer. It has to be accurately aligned and must be capable of scanning two distances so that the path difference corresponds to a known value. A number of factors associated with the moving mirror need to be considered when evaluating an infrared spectrum.

The interferogram is an analogue signal at the detector that has to be digitized in order that the Fourier-transformation into a conventional spectrum can be carried out. There are two particular sources of error in transforming the digitized information on the interferogram into a spectrum. First, the transformation carried out in practice involves an integration stage over a finite displacement rather than over an infinite displacement. The mathematical process of Fourier-transformation assumes infinite boundaries. The consequence of this necessary approximation is that the apparent lineshape of a spectral line may be as shown in Figure 2.6, where the main band area has a series of negative and positive side lobes (or pods) with diminishing amplitudes.

The process of *apodization* is the removal of the side lobes (or pods) by multiplying the interferogram by a suitable function before the Fourier-transformation is carried out. A suitable function must cause the intensity of the interferogram to fall smoothly to zero at its ends. Most FTIR spectrometers offer a choice of apodization options and a good general purpose apodization function is the cosine function, as follows:

$$F(D) = [1 + \cos\ (\pi D)]/2 \tag{2.3}$$

where D is the optical path difference. This cosine function provides a good compromise between reduction in oscillations and deterioration in spectral resolution. When accurate band shapes are required, more sophisticated mathematical functions may be needed.

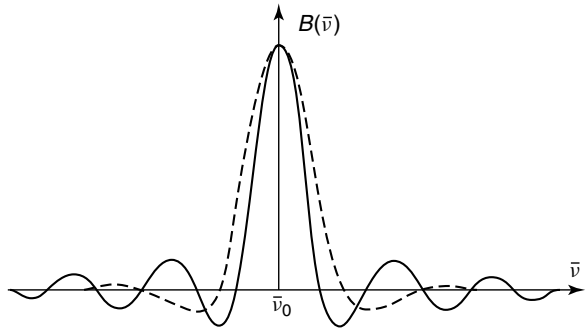

Figure 2.6 Instrument lineshape without apodization. Reproduced with permission from Barnes, A. J. and Orville-Thomas, W. J. (Eds), *Vibrational Spectroscopy – Modern Trends*, Elsevier, Amsterdam, Figure 3, p. 55 (1977).

Another source of error arises if the sample intervals are not exactly the same on each side of the maxima corresponding to zero path differences. Phase correction is required and this correction procedure ensures that the sample intervals are the same on each side of the first interval and should correspond to a path difference of zero.

The resolution for an FTIR instrument is limited by the maximum path difference between the two beams. The limiting resolution in wavenumbers (cm^{-1}) is the reciprocal of the pathlength difference (cm). For example, a pathlength difference of 10 cm is required to achieve a limiting resolution of 0.1 cm^{-1}. This simple calculation appears to show that it is easy to achieve high resolution. Unfortunately, this is not the case since the precision of the optics and mirror movement mechanism become more difficult to achieve at longer displacements of pathlengths.

SAQ 2.1

An FTIR spectrometer is used to record a single-beam spectrum from a single scan with a difference in pathlength (δ) of 100 mm.

(a) What is the limiting resolution in units of cm^{-1}?

(b) How could a limiting resolution of 0.02 cm^{-1} be achieved?

2.3.5 Signal-Averaging

The main advantage of rapid-scanning instruments is the ability to increase the signal-to-noise ratio (SNR) by signal-averaging, leading to an increase of

signal-to-noise proportional to the square root of the time, as follows:

$$\text{SNR} \propto n^{1/2} \tag{2.4}$$

There are diminishing returns for signal-averaging in that it takes an increasingly longer time to achieve greater and greater improvement. The accumulation of a large number of repeat scans makes greater demands on the instrument if it is to exactly reproduce the conditions. It is normal to incorporate a laser monochromatic source in the beam of the continuous source. The laser beam produces standard fringes which can 'line-up' successive scans accurately and can determine and control the displacement of the moving mirror at all times.

2.3.6 Advantages

FTIR instruments have several significant advantages over older dispersive instruments. Two of these are the Fellgett (or multiplex) advantage and the Jacquinot (or throughput) advantage. The *Fellgett advantage* is due to an improvement in the SNR per unit time, proportional to the square root of the number of resolution elements being monitored. This results from the large number of resolution elements being monitored simultaneously. In addition, because FTIR spectrometry does not require the use of a slit or other restricting device, the total source output can be passed through the sample continuously. This results in a substantial gain in energy at the detector, hence translating to higher signals and improved SNRs. This is known as *Jacquinot's advantage*.

Another strength of FTIR spectrometry is its *speed advantage*. The mirror has the ability to move short distances quite rapidly, and this, together with the SNR improvements due to the Fellgett and Jacquinot advantages, make it possible to obtain spectra on a millisecond timescale. In interferometry, the factor which determines the precision of the position of an infrared band is the precision with which the scanning mirror position is known. By using a helium–neon laser as a reference, the mirror position is known with high precision.

2.3.7 Computers

The computer forms a crucial component of modern infrared instruments and performs a number of functions. The computer controls the instrument, for example, it sets scan speeds and scanning limits, and starts and stops scanning. It reads spectra into the computer memory from the instrument as the spectrum is scanned; this means that the spectrum is digitized. Spectra may be manipulated using the computer, for example, by adding and subtracting spectra or expanding areas of the spectrum of interest. The computer is also used to scan the spectra continuously and average or add the result in the computer memory. Complex analyses may be automatically carried out by following a set of pre-programmed commands (described later in Chapter 3). The computer is also used to plot the spectra.

2.3.8 Spectra

Early infrared instruments recorded percentage transmittance over a linear wavelength range. It is now unusual to use wavelength for routine samples and the wavenumber scale is commonly used. The output from the instrument is referred to as a *spectrum*. Most commercial instruments present a spectrum with the wavenumber decreasing from left to right.

The infrared spectrum can be divided into three main regions: the *far-infrared* (<400 cm^{-1}), the *mid-infrared* (4000–400 cm^{-1}) and the *near-infrared* (13 000–4000 cm^{-1}). These regions will be described later in more detail in Chapter 3. Many infrared applications employ the mid-infrared region, but the near- and far-infrared regions also provide important information about certain materials. Generally, there are less infrared bands in the 4000–1800 cm^{-1} region with many bands between 1800 and 400 cm^{-1}. Sometimes, the scale is changed so that the region between 4000 and 1800 cm^{-1} is contracted and the region between 1800 and 400 cm^{-1} is expanded to emphasize features of interest.

The ordinate scale may be presented in % transmittance with 100% at the top of the spectrum. It is commonplace to have a choice of absorbance or transmittance as a measure of band intensity. The relationship between these two quantities will be described in Chapter 3. Figures 2.7 and 2.8 show the infrared spectra of lactic acid and illustrate the difference in appearance between absorbance and

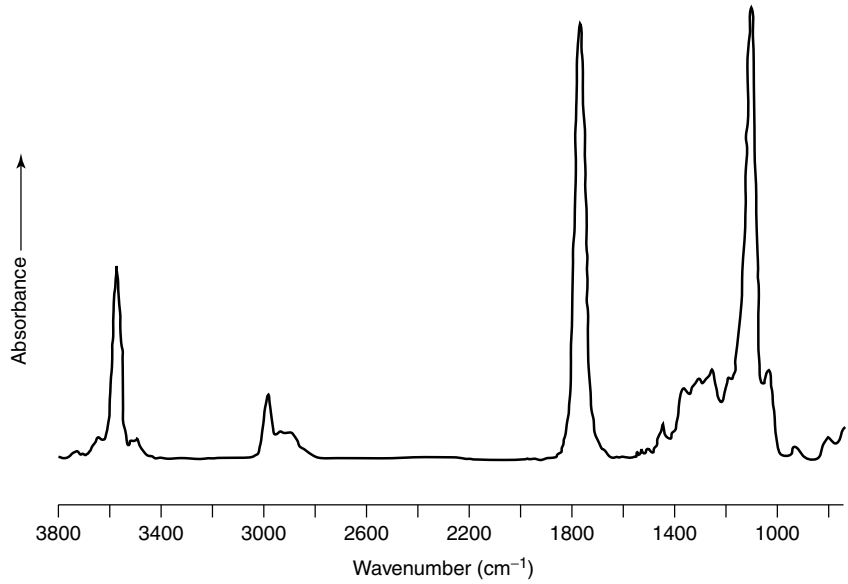

Figure 2.7 Absorbance spectrum of lactic acid. From Stuart, B., *Biological Applications of Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1997. © University of Greenwich, and reproduced by permission of the University of Greenwich.

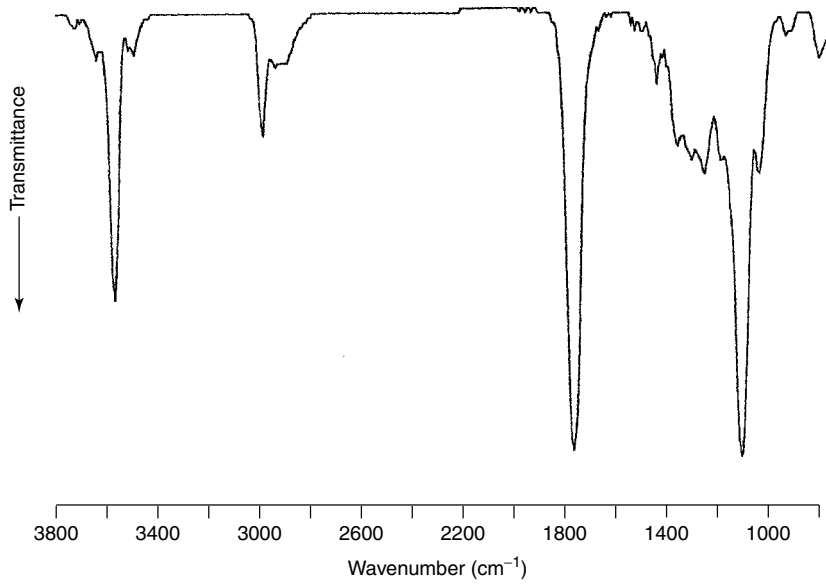

Figure 2.8 Transmittance spectrum of lactic acid. From Stuart, B., *Biological Applications of Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1997. © University of Greenwich, and reproduced by permission of the University of Greenwich.

transmittance spectra. It almost comes down to personal preference which of the two modes to use, but the transmittance is traditionally used for spectral interpretation, while absorbance is used for quantitative work.

2.4 Transmission Methods

Transmission spectroscopy is the oldest and most straightforward infrared method. This technique is based upon the absorption of infrared radiation at specific wavelengths as it passes through a sample. It is possible to analyse samples in the liquid, solid or gaseous forms when using this approach.

2.4.1 Liquids and Solutions

There are several different types of transmission solution cells available. Fixed-pathlength sealed cells are useful for volatile liquids, but cannot be taken apart for cleaning. Semi-permanent cells are demountable so that the windows can be cleaned. A semi-permanent cell is illustrated in Figure 2.9. The spacer is usually made of polytetrafluoroethylene (PTFE, known as 'Teflon') and is available in a variety of thicknesses, hence allowing one cell to be used for various pathlengths. Variable pathlength cells incorporate a mechanism for continuously adjusting the pathlength, while a vernier scale allows accurate adjustment. All of these cell

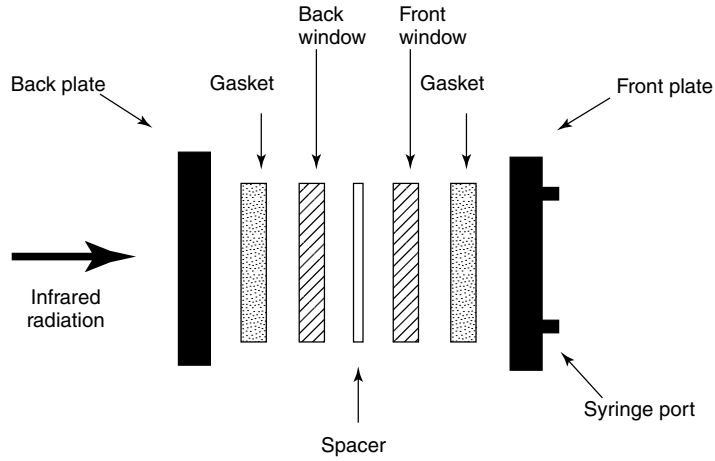

Figure 2.9 Schematic of a typical semi-permanent liquid cell. From Stuart, B., *Biological Applications of Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1997. © University of Greenwich, and reproduced by permission of the University of Greenwich.

types are filled by using a syringe and the syringe ports are sealed with PTFE plugs before sampling.

DQ 2.1

Which type of solution cell would you consider to be the easiest to maintain?

Answer

*The **demountable** is by far the easiest to maintain as it can be readily dismantled and cleaned. The windows can be repolished, a new spacer supplied and the cell reassembled. The **permanent** cells are difficult to clean and can become damaged by water. The pathlengths need to calibrated regularly if quantitative work is to be undertaken. Variable pathlength cells suffer from similar disadvantages and they are difficult to take apart. The calibration therefore suffers and the cells have to be calibrated regularly.*

An important consideration in the choice of infrared cells is the type of window material. The latter must be transparent to the incident infrared radiation and alkali halides are normally used in transmission methods. The cheapest material is sodium chloride (NaCl), but other commonly used materials are listed in Table 2.1.

Certain difficulties arise when using water as a solvent in infrared spectroscopy. The infrared modes of water are very intense and may overlap with the sample modes of interest. This problem may be overcome by substituting water with deuterium oxide (D_2O). The infrared modes of D_2O occur at different wavenumbers to those observed for water because of the mass dependence of

Table 2.1 Summary of some optical materials used in transmission infrared spectroscopy. From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich

Window material	Useful range (cm^{-1})	Refractive index	Properties
NaCl	40 000–600	1.5	Soluble in water; slightly soluble in alcohol; low cost; fair resistance to mechanical and thermal shock; easily polished
KBr	43 500–400	1.5	Soluble in water and alcohol; slightly soluble in ether; hygroscopic; good resistance to mechanical and thermal shock
CaF_2	77 000–900	1.4	Insoluble in water; resists most acids and bases; does not fog; useful for high-pressure work
BaF_2	66 666–800	1.5	Insoluble in water; soluble in acids and NH_4Cl; does not fog; sensitive to thermal and mechanical shock
KCl	33 000–400	1.5	Similar properties to NaCl but less soluble; hygroscopic
CsBr	42 000–250	1.7	Soluble in water and acids; hygroscopic
CsI	42 000–200	1.7	Soluble in water and alcohol; hygroscopic

the vibrational wavenumber. Table 2.2 lists the characteristic bands observed for both H_2O and D_2O. Where water is used as a solvent, NaCl cannot be employed as a infrared window material as it is soluble in water. Small pathlengths ($\sim$ 0.010 mm) are available in liquid cells and help reduce the intensities of the very strong infrared modes produced in the water spectrum. The small pathlength also produces a small sample cavity, hence allowing samples in milligram quantities to be examined.

SAQ 2.2

What would be an appropriate material for liquid cell windows if an aqueous solution at pH 7 is to be examined?

Liquid films provide a quick method of examining liquid samples. A drop of liquid may be sandwiched between two infrared plates, which are then mounted in a cell holder.

Table 2.2 The major infrared bands of water and deuterium oxide. From Stuart, B., *Biological Applications of Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1997. © University of Greenwich, and reproduced by permission of the University of Greenwich

Wavenumber (cm^{-1})	Assignment
3920	O–H stretching
3490	O–H stretching
3280	O–H stretching
1645	H–O–H bending
2900	O–D stretching
2540	O–D stretching
2450	O–D stretching
1215	D–O–D bending

DQ 2.2

The method of liquid films is normally not used for volatile (with a boiling point less than 100°C) liquids. Why would this be necessary?

Answer

A common problem encountered in obtaining good quality spectra from liquid films is sample volatility. When the spectrum of a volatile sample is recorded, it progressively becomes weaker because evaporation takes place during the recording period. Liquids with boiling points below 100°C should be recorded in solution or in a short-pathlength sealed cell.

Before producing an infrared sample in solution, a suitable solvent must be chosen. In selecting a solvent for a sample, the following factors need to be considered: it has to dissolve the compound, it should be as non-polar as possible to minimize solute–solvent interactions, and it should not strongly absorb infrared radiation.

If quantitative analysis of a sample is required, it is necessary to use a cell of known pathlength. A guide to pathlength selection for different solution concentrations is shown in Table 2.3.

2.4.2 Solids

There are three general methods used for examining solid samples in transmission infrared spectroscopy; i.e. alkali halide discs, mulls and films. The choice of method depends very much on the nature of the sample to be examined. The use of alkali halide discs involves mixing a solid sample with a dry alkali halide powder. The mixture is usually ground with an agate mortar and pestle and

Table 2.3 Pathlength selection for solution cells. From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich

Concentration (%)	Pathlength (mm)
>10	0.05
1–10	0.1
0.1–1	0.2
< 0.1	>0.5

subjected to a pressure of about 10 ton in^{-2} (1.575×10^5 kg m^{-2}) in an evacuated die. This sinters the mixture and produces a clear transparent disc. The most commonly used alkali halide is potassium bromide (KBr), which is completely transparent in the mid-infrared region. Certain factors need to be considered when preparing alkali halide discs. The ratio of the sample to alkali halide is important; surprisingly little sample is needed and around 2 to 3 mg of sample with about 200 mg of halide is sufficient. The disc must not be too thick or too thin; thin discs are fragile and difficult to handle, while thick discs transmit too little radiation. A disc of about 1 cm diameter made from about 200 mg of material usually results in a good thickness of about 1 mm. If the crystal size of the sample is too large, excessive scattering of radiation results, particularly so at high wavenumbers (this is known as the *Christiansen effect*). The crystal size must be reduced, normally by grinding the solid using a mortar and pestle. If the alkali halide is not perfectly dry, bands due to water appear in the spectrum. Contributions due to water are difficult to avoid, and so the alkali halide should be kept desiccated and warm prior to use in order to minimize this effect.

The mull method for solid samples involves grinding the sample and then suspending this (about 50 mg) in one to two drops of a mulling agent. This is followed by further grinding until a smooth paste is obtained. The most commonly used mulling agent is Nujol (liquid paraffin), with its spectrum being shown in Figure 2.10. Although the mull method is quick and easy, there are some experimental factors to consider. The ratio of the sample to mulling agent must be correct. Too little sample, and there will be no sign of the sample in the spectrum. Too much sample and a thick paste will be produced and no radiation will be transmitted. A rough guide to mull preparation is to use a micro-spatula tip of sample to two to three drops of mulling agent. If the crystal size of the sample is too large, this leads to scattering of radiation, which gets worse at the high-wavenumber end of the spectrum. If the mull is not spread over the whole plate area, the beam of radiation

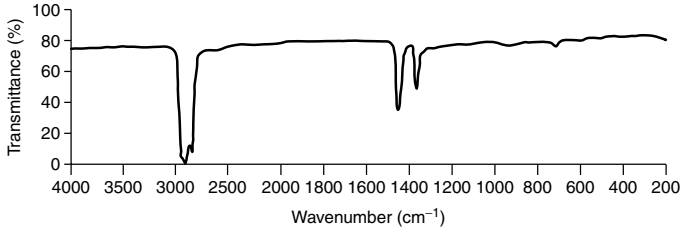

Figure 2.10 Infrared spectrum of Nujol (liquid paraffin). From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

passes part through the mull and only part through the plates, hence producing a distorted spectrum. The amount of sample placed between the infrared plates is an important factor; too little leads to a very weak spectrum showing only the strongest absorption bands. Too much mull leads to poor transmission of radiation so that the baseline may be at 50% or less.

It is sometimes possible to reduce the energy of a reference beam to a similar extent by use of an *attenuator*. Beam attenuators are placed in the sample compartment, working somewhat like a venetian blind, and the amount of radiation passing to the detector may be adjusted.

SAQ 2.3

The spectrum of a mull is shown in Figure 2.11. What is the problem with the mull produced and how would one go about remedying the problem?

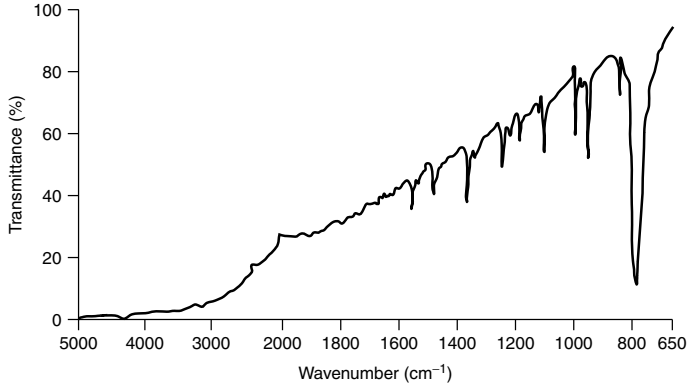

Figure 2.11 Infrared spectrum of a mull (cf. SAQ 2.3). From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

Films can be produced by either solvent casting or by melt casting. In solvent casting, the sample is dissolved in an appropriate solvent (the concentration depends on the required film thickness). A solvent needs to be chosen which not only dissolves the sample, but will also produce a uniform film. The solution is poured onto a levelled glass plate (such as a microscope slide) or a metal plate and spread to uniform thickness. The solvent may then be evaporated in an oven and, once dry, the film can be stripped from the plate. However, care must be taken as the heating of samples may cause degradation. Alternatively, it is possible to cast a film straight onto the infrared window to be used. Solid samples which melt at relatively low temperatures without decomposition can be prepared by melt casting. A film is prepared by 'hot-pressing' the sample in a hydraulic press between heated metal plates.

2.4.3 Gases

Gases have densities which are several orders of magnitude less than liquids, and hence pathlengths must be correspondingly greater, usually 10 cm or longer [2]. A typical gas cell is shown in Figure 2.12. The walls are of glass or brass, with the usual choice of windows. The cells can be filled by flushing or from a gas line. To analyse complex mixtures and trace impurities, longer pathlengths are necessary. As the sample compartment size in the instrument is limited, a multi-reflection gas cell is necessary to produce higher pathlengths. In such a cell, the infrared beam is deflected by a series of mirrors which reflect the beam back and forth many times until it exits the cell after having travelled the required

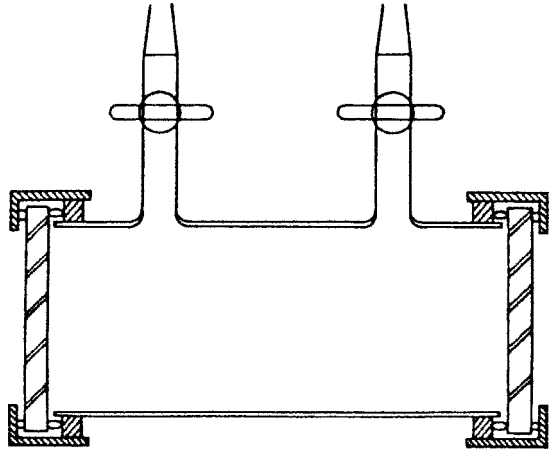

Figure 2.12 Schematic of a typical infrared gas cell. From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

equivalent pathlength. This type of cell allows a pathlength of up to 40 m to be attained.

2.4.4 Pathlength Calibration

When using transmission cells it can be useful to know precisely the pathlength of the cell, particularly for quantitative measurements. The cell pathlength can be measured by the method of counting interference fringes. If an empty cell with parallel windows is placed in the spectrometer and a wavelength range scanned, an interference pattern similar to that shown in Figure 2.13 will be obtained. The amplitude of the waveform will vary from 2 to 15%, depending on the state of the windows. The relationship between the pathlength of the cell, L, and the peak-to-peak fringes is given by the following:

$$L = \frac{n}{2(\bar{\nu}_1 - \bar{\nu}_2)} \tag{2.5}$$

where n is the number of complete peak-to-peak fringes between two maxima (or minima) at $\bar{\nu}_1$ and $\bar{\nu}_2$. If the spectrometer is calibrated in wavelengths, the n in Equation (2.5) can be converted to a more convenient form:

$$L = \frac{n(\lambda_1 \times \lambda_2)}{2(\lambda_1 - \lambda_2)} \tag{2.6}$$

where the values of the wavelengths, λ, are expressed in cm.

When a beam of radiation is directed into the face of a cell, most of the radiation will pass straight through (Figure 2.14, beam A). Some of the radiation will undergo a double reflection (beam B) and will, therefore, have travelled an extra distance $2L$ compared to beam A. If this extra distance is equal to a whole number of wavelengths, then beams A and B will be in-phase and the intensity of the transmitted beam (A + B) will be at a maximum. The intensity will be at a minimum when the two component beams are half a wavelength out-of-phase.

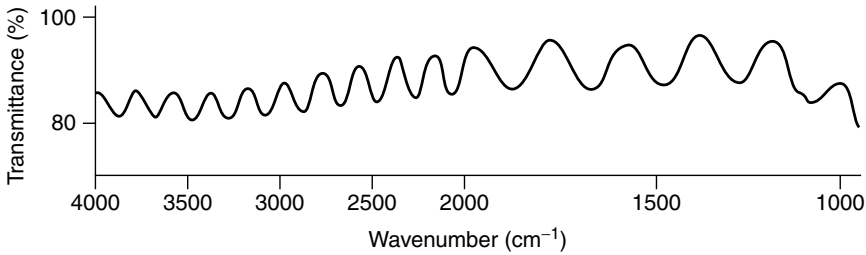

Figure 2.13 Interference pattern recorded with an empty cell in the sample beam. From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

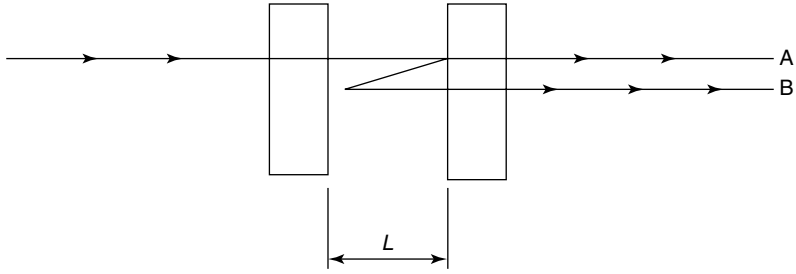

Figure 2.14 Beam of radiation passing through an empty cell.

SAQ 2.4

Using the interference pattern given in Figure 2.13, calculate the pathlength of the cell.

2.5 Reflectance Methods

Reflectance techniques may be used for samples that are difficult to analyse by the conventional transmittance methods. Reflectance methods can be divided into two categories. Internal reflectance measurements can be made by using an attenuated total reflectance cell in contact with the sample. There is also a variety of external reflectance measurements which involve an infrared beam reflected directly from the sample surface.

2.5.1 Attenuated Total Reflectance Spectroscopy

Attenuated total reflectance (ATR) spectroscopy utilizes the phenomenon of *total internal reflection* (Figure 2.15). A beam of radiation entering a crystal will undergo total internal reflection when the angle of incidence at the interface between the sample and crystal is greater than the critical angle, where the latter is a function of the refractive indices of the two surfaces. The beam penetrates a fraction of a wavelength beyond the reflecting surface and when a material that selectively absorbs radiation is in close contact with the reflecting surface, the beam loses energy at the wavelength where the material absorbs. The resultant attenuated radiation is measured and plotted as a function of wavelength by the spectrometer and gives rise to the absorption spectral characteristics of the sample.

The depth of penetration in ATR spectroscopy is a function of the wavelength, λ, the refractive index of the crystal, n_2, and the angle of incident radiation, θ. The

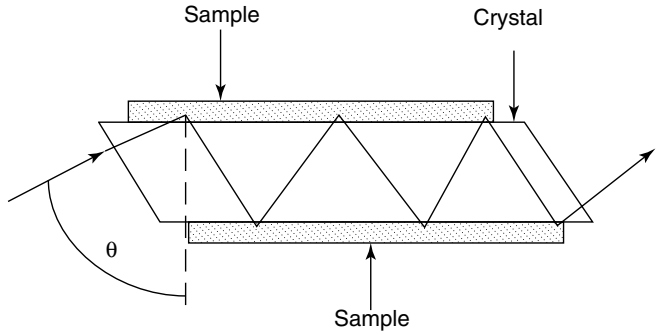

Figure 2.15 Schematic of a typical attenuated total reflectance cell. From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

depth of penetration, d_p, for a non-absorbing medium is given by the following:

$$d_p = (\lambda/n_1)/\left\{2\pi[\sin\theta - (n_1/n_2)^2]^{1/2}\right\} \tag{2.7}$$

where n_1 is the refractive index of the sample.

The crystals used in ATR cells are made from materials that have low solubility in water and are of a very high refractive index. Such materials include zinc selenide (ZnSe), germanium (Ge) and thallium–iodide (KRS-5). The properties of these commonly used materials for ATR crystals are summarized in Table 2.4.

Different designs of ATR cells allow both liquid and solid samples to be examined. It is also possible to set up a flow-through ATR cell by including an inlet and outlet in the apparatus. This allows for the continuous flow of solutions through the cell and permits spectral changes to be monitored with

Table 2.4 Materials used as ATR crystals and their properties. From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich

Window material	Useful range (cm^{-1})	Refractive index	Properties
KRS-5 (thallium iodide)	17 000–250	2.4	Soluble in bases; slightly soluble in water; insoluble in acids; soft; highly toxic (handle with gloves)
ZnSe	20 000–500	2.4	Insoluble in water, organic solvents, dilute acids and bases
Ge	5000–550	4.0	Insoluble in water; very brittle

time. Multiple internal reflectance (MIR) and ATR are similar techniques, but MIR produces more intense spectra from multiple reflections. While a prism is usually used in ATR work, MIR uses specially shaped crystals that cause many internal reflections, typically 25 or more.

SAQ 2.5

The spectrum of a polymer film (refractive index, 1.5) was produced by using an ATR cell made of KRS-5 (refractive index, 2.4). If the incident radiation enters the cell crystal at an angle of 60°, what is the depth of penetration into the sample surface at:

(a) 1000 cm^{-1}

(b) 1500 cm^{-1}

(c) 3000 cm^{-1}?

2.5.2 Specular Reflectance Spectroscopy

In external reflectance, incident radiation is focused onto the sample and two forms of reflectance can occur, i.e. *specular* and *diffuse*. External reflectance measures the radiation reflected from a surface. The material must, therefore, be reflective or be attached to a reflective backing. A particularly appropriate application for this technique is the study of surfaces.

Specular reflectance occurs when the reflected angle of radiation equals the angle of incidence (Figure 2.16). The amount of light reflected depends on the angle of incidence, the refractive index, surface roughness and absorption properties of the sample. For most materials, the reflected energy is only 5–10%, but in regions of strong absorptions, the reflected intensity is greater. The resultant data appear different from normal transmission spectra, as 'derivative-like' bands result from the superposition of the normal extinction coefficient spectrum with the refractive index dispersion (based upon Fresnel's relationships). However, the reflectance spectrum can be corrected by using a *Kramers–Kronig transformation* (K–K transformation). The corrected spectrum then appears like the familiar transmission spectrum.

Increased pathlengths through thin coatings can be achieved by using grazing angles of incidence (up to 85°). Grazing angle sampling accessories allow measurements to be made on samples over a wide range of angles of incidence. Solid samples, particularly coatings on reflective surfaces, are simply placed on a flat surface. The technique is also commonly used for liquid samples that can be poured into a 'Teflon' trough. Oriented films on the liquid surface can be investigated by using this method.

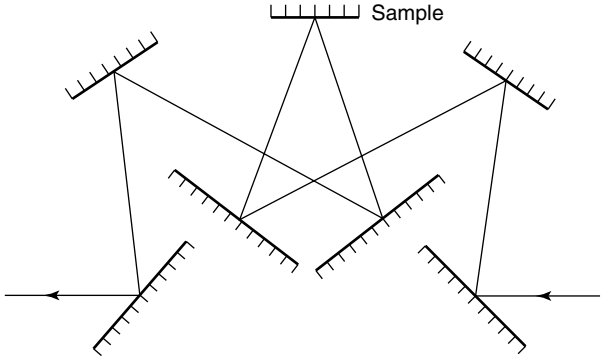

Figure 2.16 Illustration of specular reflectance.

2.5.3 Diffuse Reflectance Spectroscopy

In external reflectance, the energy that penetrates one or more particles is reflected in all directions and this component is called *diffuse reflectance*. In the diffuse reflectance (infrared) technique, commonly called DRIFT, a powdered sample is mixed with KBr powder. The DRIFT cell reflects radiation to the powder and collects the energy reflected back over a large angle. Diffusely scattered light can be collected directly from material in a sampling cup or, alternatively, from material collected by using an abrasive sampling pad. DRIFT is particularly useful for sampling powders or fibres. Figure 2.17 illustrates diffuse reflectance from the surface of a sample.

Kubelka and Munk developed a theory describing the diffuse reflectance process for powdered samples which relates the sample concentration to the scattered radiation intensity. The Kubelka–Munk equation is as follows:

$$(1 - R)^2/2R = c/k \tag{2.8}$$

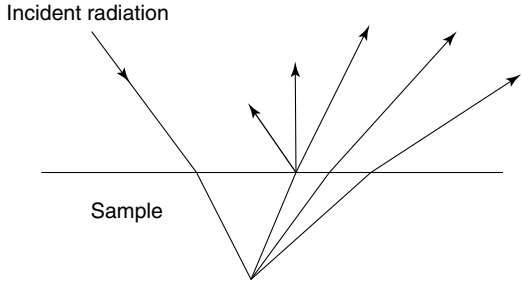

Figure 2.17 Illustration of diffuse reflectance.

where R is the absolute reflectance of the layer, c is the concentration and k is the molar absorption coefficient. An alternative relationship between the concentration and the reflected intensity is now widely used in near-infrared diffuse reflectance spectroscopy, namely:

$$\log (1/R) = k'c \tag{2.9}$$

where k' is a constant.

2.5.4 Photoacoustic Spectroscopy

Photoacoustic spectroscopy (PAS) is a non-invasive reflectance technique with penetration depths in the range from microns down to several molecular monolayers. Gaseous, liquid or solid samples can be measured by using PAS and the technique is particularly useful for highly absorbing samples. The photoacoustic effect occurs when intensity-modulated light is absorbed by the surface of a sample located in an acoustically isolated chamber filled with an inert gas. A spectrum is obtained by measuring the heat generated from the sample due to a re-absorption process. The sample absorbs photons of the modulated radiation,

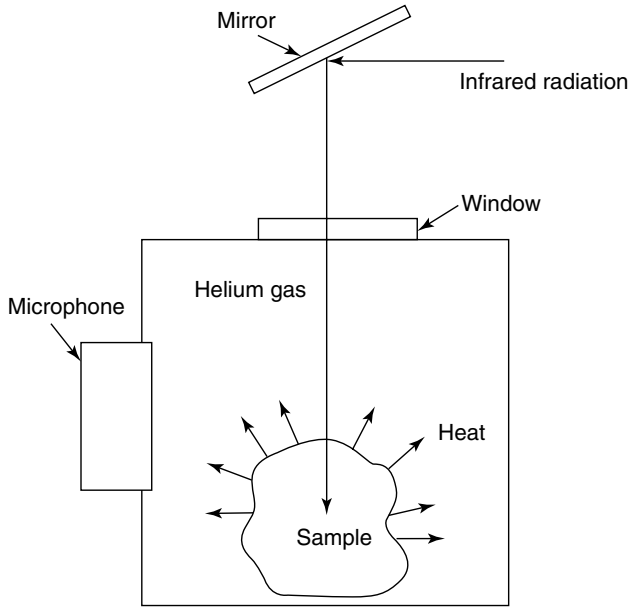

Figure 2.18 Schematic of a typical photoacoustic spectroscopy cell. From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

which have energies corresponding to the vibrational states of the molecules. The absorbed energy is released in the form of heat generated by the sample, which causes temperature fluctuations and, subsequently, periodic acoustic waves. A microphone detects the resulting pressure changes, which are then converted to electrical signals. Fourier-transformation of the resulting signal produces a characteristic infrared spectrum. Figure 2.18 shows a schematic diagram of a PAS cell.

2.6 Microsampling Methods

It is possible to combine an infrared spectrometer with a microscope facility in order to study very small samples [3–6]. In recent years, there have been considerable advances in FTIR microscopy, with samples of the order of microns being characterized. In FTIR microscopy, the microscope sits above the FTIR sampling compartment. Figure 2.19 illustrates the layout of a typical infrared microscope assembly. Infrared radiation from the spectrometer is focused onto a sample placed on a standard microscope $x-y$ stage. After passing through the sample, the infrared beam is collected by a Cassegrain objective which produces an image of the sample within the barrel of the microscope. A variable aperture is placed in this image plane. The radiation is then focused on to a small-area mercury cadmium telluride (MCT) detector by another Cassegrain condenser. The microscope also contains glass objectives to allow visual inspection of the sample. In addition, by switching mirrors in the optical train, the microscope can be converted from transmission mode to reflectance mode.

If a microscope facility is not available, there are other special sampling accessories available to allow examination of microgram or microlitre amounts. This is accomplished by using a *beam condenser* so that as much as possible of the beam passes through the sample. Microcells are available with volumes of around 4 μl and pathlengths up to 1 mm. A *diamond anvil cell* (DAC) uses two diamonds to compress a sample to a thickness suitable for measurement and increase the surface area. This technique can be used at normal atmospheric pressures, but it may also be employed to study samples under high pressures and improve the quality of the spectrum of trace samples. Alternatively, a multiple internal reflectance cell may also be used as this technique can produce stronger spectra.

Infrared imaging using FTIR microspectroscopic techniques has emerged as an effective approach for studying complex or heterogeneous specimens [7]. The technique can be used to produce a two- or three-dimensional ‘picture’ of the properties of a sample. This is achievable because, instead of reading the signal of

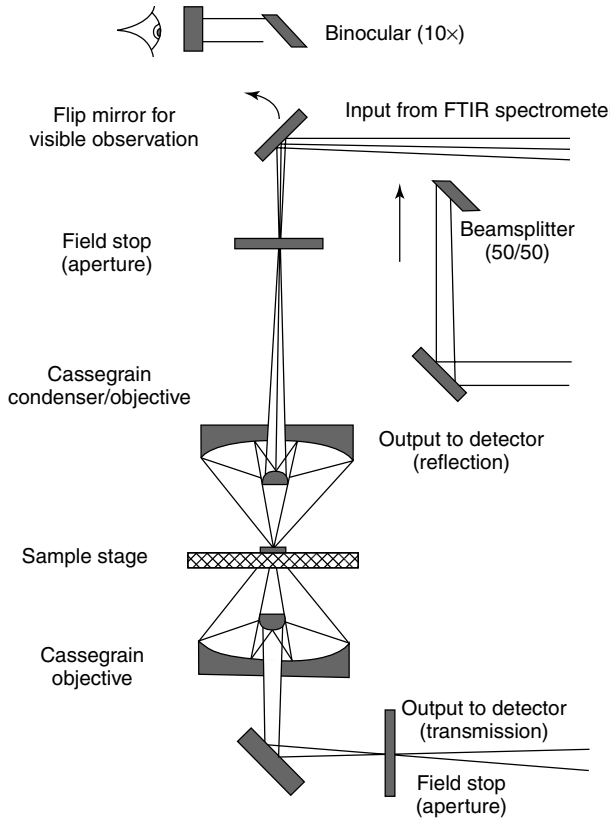

Figure 2.19 Layout of a typical FTIR microspectrometer. Reprinted from Katon, J. E., Sommer, A. J. and Lang, P. L., *Applied Spectroscopy Reviews*, Vol. 25, pp. 173–211 (1989–1990), courtesy of Marcel Dekker, Inc.

only one detector as in conventional FTIR spectroscopy, a large number of detector elements are read during the acquisition of spectra. This is possible due to the development of focal plane array (FPA) detectors. Currently, a step-scanning approach is used which means that that the moving mirror does not move continuously during data acquisition, but waits for each detector readout to be completed before moving on to the next position. This allows thousands of interferograms to be collected simultaneously and then transformed into infrared spectra.

Figure 2.20 illustrates the general layout of an FTIR imaging microspectrometer. The infrared beam from a Michelson interferometer is focused onto a sample with a reflective Cassegrain condenser. The light transmitted is collected by a Cassegrain objective and then focused onto an FPA detector. The imaging process

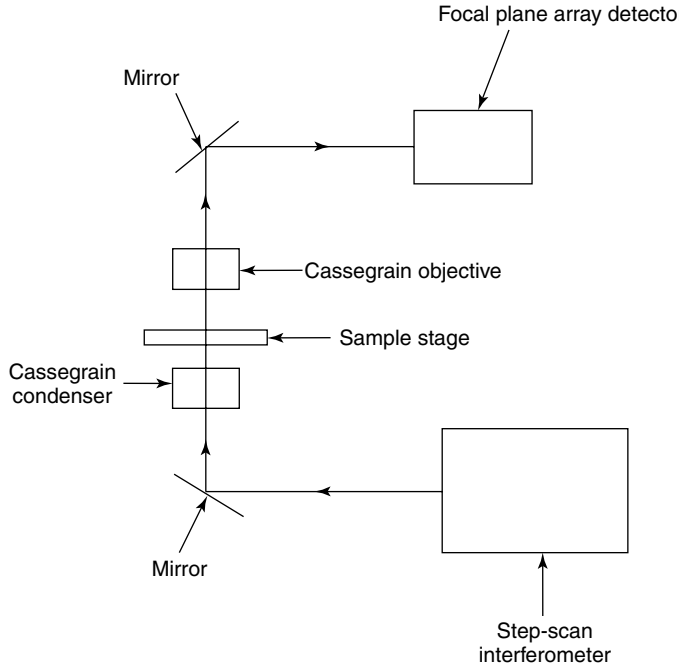

Figure 2.20 Layout of a typical FTIR imaging microspectrometer.

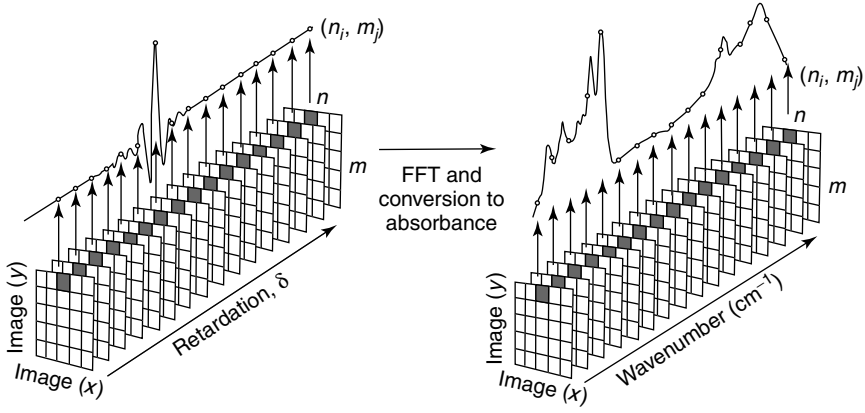

Figure 2.21 FTIR imaging data set. From Kidder, L. H., Levin, I. W. and Lewis, E. N., 'Infrared Spectroscopic Imaging Microscopy: Applications to Biological Systems', in *Proceedings of the 11th International Fourier Transform Spectroscopy Conference*, Athens, GA, USA, August 10–15, 1997, de Haseth, J. A. (Ed.), Figure 1, p. 148, American Institute of Physics, Melville, New York, 1998, pp. 148–158. Reproduced by permission of American Institute of Physics.

is illustrated in Figure 2.21. The data are collected as interferograms with each pixel on the array having a response determined by its corresponding location on the sample. Each point of the interferogram represents a particular moving mirror position and the spectral data are obtained by performing a Fourier-transform for each pixel on the array. Thus, each pixel (or spatial location) is represented by an infrared spectrum.

2.7 Chromatography–Infrared Spectroscopy

Infrared spectroscopy may be combined with each of a number of possible chromatographic techniques, with gas chromatography–infrared spectroscopy (GC–IR) being the most widely used [8, 9]. GC–IR allows for the identification of the components eluting from a gas chromatograph. In GC, the sample in a gaseous mobile phase is passed through a column containing a liquid or solid stationary phase. The retention of the sample depends on the degree of interaction with the stationary phase and its volatility: the higher the affinity of the sample for the stationary phase, then the more the sample partitions into that phase and the longer it takes before it passes through the chromatograph. The sample is introduced into the column, housed in an oven, via injection at one end and a detector monitors the effluent at the other end. A common method for coupling a gas chromatograph to an FTIR spectrometer is to use a light pipe, i.e. a heated flow cell which allows the continuous scanning of the effluent emerging from the GC column. Figure 2.22 shows a schematic diagram of a typical GC–IR system.

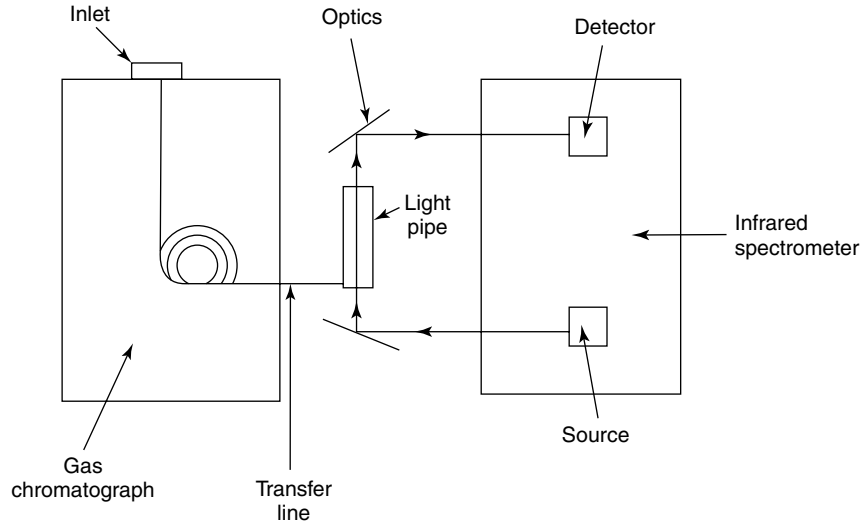

Figure 2.22 Layout of a typical GC–IR system.

The nature of this technique requires that interferograms are collected over short time intervals. Data can be displayed in real time and are commonly monitored as the changing spectrum of the GC effluent and the changing infrared absorption as a function of time. The latter is known as a *Gram–Schmidt chromatogram*.

Liquid chromatography (LC) may also be used in conjunction with infrared spectroscopy [10]. In this technique, the effluent from a liquid chromatograph is passed through a liquid flow-through cell. Supercritical fluid chromatography (SFC), where supercritical CO_2 is commonly used as a mobile phase, can be used with FTIR spectroscopy to improve detection limits.

2.8 Thermal Analysis–Infrared Spectroscopy

Infrared spectrometers may also be combined with thermal analysis instrumentation. Thermal analysis methods provide information about the temperature-dependent physical properties of materials. However, it is not always possible to gain information about the chemical changes associated with changes in temperature by using standard thermal analysis equipment. It is possible to combine thermal analysis apparatus with an infrared spectrometer in order to obtain a complete picture of the chemical and physical changes occurring in various thermal processes [11, 12].

The most common approach is to combine FTIR spectroscopy with a thermal method such as thermogravimetric analysis (TGA) to obtain an evolved gas analysis (EGA). The latter involves the measurement and characterization of the

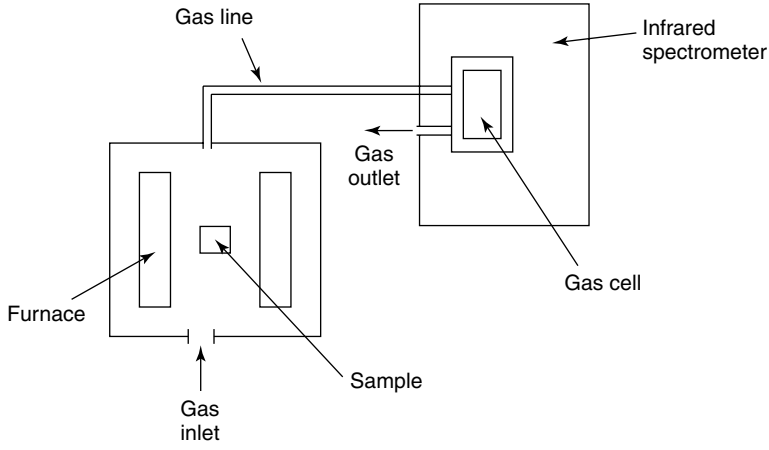

Figure 2.23 Layout of a typical thermal analysis–infrared spectroscopy system.

gaseous products which evolve from a sample when it is heated. Figure 2.23 presents a schematic layout of a typical thermal analysis–infrared spectroscopy system. In this, a sample is placed in a furnace while being suspended from a sensitive balance. The change in sample mass is recorded while the sample is maintained either at a required temperature or while being subjected to a programmed heating sequence. A TGA curve may be plotted as sample mass loss as a function of temperature or in a differential form where the change in sample mass with time is plotted as a function of temperature. The evolved gases can be carried from the furnace to the spectrometer where they can be examined in a long-pathlength gas cell. Data may be illustrated as a function of time by using a Gram–Schmidt plot.

2.9 Other Techniques

Variable-temperature cells, which are controlled to 0.1°C in the range −180 to 250°C, may be used in infrared spectrometers. An electrical heating system is used for temperatures above ambient, and liquid nitrogen with a heater for low temperatures. These cells can be used to study phase transitions and the kinetics of reactions. As well as transmission temperature cells, variable-temperature ATR cells and temperature cells for microsampling are available.

Infrared emission spectroscopy may be carried out by using a heated sample located in the emission port of the FTIR spectrometer as the radiation source.

Optical fibres may be used in conjunction with infrared spectrometers to carry out remote measurements. The fibres transfer the signal to and from a sensing probe and are made of materials that are flexible and 'infrared-transparent'.

For some samples, dipole moment changes may be in a fixed direction during a molecular vibration and, as such, can only be induced when the infrared radiation is polarized in that direction. Polarized infrared radiation can be produced by using a polarizer consisting of a fine grating of parallel metal wires. This approach is known as *linear infrared dichroism* [13].

SAQ 2.6

Which sampling technique would be the most appropriate in each of the cases listed below?

(a) A 1 g sample of white powder.

(b) A 10 μg sample of animal tissue.

(c) A powder containing a mixture of amphetamines.

Summary

Various aspects of the instrumentation used in infrared spectroscopy were dealt with in this chapter. Traditional dispersive spectrometers were described. The operation and capabilities of Fourier-transform infrared spectrometers were also discussed. Transmission methods for obtaining infrared spectra were also examined. The sampling methods which can be used for solids, solutions, liquids and gases were presented. The different reflectance methods that are now widely available, such as ATR spectroscopy, specular reflectance and diffuse reflectance, along with photoacoustic spectroscopy, were also introduced. The various microsampling techniques, which have emerged as effective methods for investigating small quantities of complex samples, were also described. Infrared spectrometers can also be used in conjunction with other analytical methods such as chromatography and thermal techniques and these were introduced in this chapter.

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Chapter 3
Spectral Analysis

Learning Objectives

- To recognize the characteristic bands that appear in the mid-infrared, near-infrared and far-infrared regions.
- To understand how hydrogen bonding affects an infrared spectrum.
- To develop a strategy for the interpretation of infrared spectra.
- To understand and use a variety of techniques to compensate for background absorption and overlapping peaks.
- To convert transmittance values to the corresponding absorbance values.
- To use the Beer–Lambert law for the quantitative analysis of samples studied using infrared spectroscopy.
- To analyse simple mixtures using their infrared spectra.
- To analyse multi-component systems using their infrared spectra.
- To recognize the calibration methods that may be applied to samples studied using infrared spectroscopy.

3.1 Introduction

Once an infrared spectrum has been recorded, the next stage of this experimental technique is interpretation. Fortunately, spectrum interpretation is simplified by the fact that the bands that appear can usually be assigned to particular parts of a molecule, producing what are known as *group frequencies*. The characteristic group frequencies observed in the mid-infrared region are discussed in this chapter. The types of molecular motions responsible for infrared bands in the near-infrared and far-infrared regions are also introduced.

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In Chapter 1, some of the factors which complicate the appearance of infrared spectra were defined, i.e. overtones and combination bands, coupling, Fermi resonance and vibration–rotation bands. Another factor, hydrogen bonding, may also contribute to notable changes in infrared spectra. The presence of this type of bonding in molecules can introduce additional, and sometimes misleading, information into the spectra. It is important to be aware of such factors before tackling the interpretation of a given spectrum.

Quantitative infrared spectroscopy can provide certain advantages over other analytical techniques. This approach may be used for the analysis of one component of a mixture, especially when the compounds in the mixture are alike chemically or have very similar physical properties (for example, structural isomers). In these instances, analysis using ultraviolet/visible spectroscopy, for instance, is difficult because the spectra of the components will be nearly identical. Chromatographic analysis may be of limited use because separation, of say isomers, is difficult to achieve. The infrared spectra of isomers are usually quite different in the *fingerprint* region. Another advantage of the infrared technique is that it can be non-destructive and requires a relatively small amount of sample.

In this present chapter, an introduction is provided on how infrared spectroscopy can be used for quantitative analysis. First, the various ways in which an infrared spectrum can be manipulated for analysis are outlined. Concentration is an important issue in quantitative analysis and the important relationships are introduced. Not only may quantitative infrared analysis be carried out on simple systems, it can also be applied to multi-component systems. Here, some straightforward examples will be used to demonstrate the analysis of the data obtained, while the calibration methods commonly applied to such infrared data will also be described.

3.2 Group Frequencies

3.2.1 Mid-Infrared Region

The mid-infrared spectrum (4000–400 cm^{-1}) can be approximately divided into four regions and the nature of a group frequency may generally be determined by the region in which it is located. The regions are generalized as follows: the X–H stretching region (4000–2500 cm^{-1}), the triple-bond region (2500–2000 cm^{-1}), the double-bond region (2000–1500 cm^{-1}) and the fingerprint region (1500–600 cm^{-1}).

The fundamental vibrations in the 4000–2500 cm^{-1} region are generally due to O–H, C–H and N–H stretching. O–H stretching produces a broad band that occurs in the range 3700–3600 cm^{-1}. By comparison, N–H stretching is usually observed between 3400 and 3300 cm^{-1}. This absorption is generally much

sharper than O–H stretching and may, therefore, be differentiated. C–H stretching bands from aliphatic compounds occur in the range 3000–2850 cm^{-1}. If the C–H bond is adjacent to a double bond or aromatic ring, the C–H stretching wavenumber increases and absorbs between 3100 and 3000 cm^{-1}.

Triple-bond stretching absorptions fall in the 2500–2000 cm^{-1} region because of the high force constants of the bonds. C≡C bonds absorb between 2300 and 2050 cm^{-1}, while the nitrile group (C≡N) occurs between 2300 and 2200 cm^{-1}. These groups may be distinguished since C≡C stretching is normally very weak, while C≡N stretching is of medium intensity. These are the most common absorptions in this region, but you may come across some X–H stretching absorptions, where X is a more massive atom such as phosphorus or silicon. These absorptions usually occur near 2400 and 2200 cm^{-1}, respectively.

The principal bands in the 2000–1500 cm^{-1} region are due to C=C and C=O stretching. Carbonyl stretching is one of the easiest absorptions to recognize in an infrared spectrum. It is usually the most intense band in the spectrum, and depending on the type of C=O bond, occurs in the 1830–1650 cm^{-1} region. Note also that metal carbonyls may absorb above 2000 cm^{-1}. C=C stretching is much weaker and occurs at around 1650 cm^{-1}, but this band is often absent for symmetry or dipole moment reasons. C=N stretching also occurs in this region and is usually stronger.

It has been assumed so far that each band in an infrared spectrum can be assigned to a particular deformation of the molecule, the movement of a group of atoms, or the bending or stretching of a particular bond. This is possible for many bands, particularly stretching vibrations of multiple bonds that are 'well behaved'. However, many vibrations are not so well behaved and may vary by hundreds of wavenumbers, even for similar molecules. This applies to most bending and skeletal vibrations, which absorb in the 1500–650 cm^{-1} region, for which small steric or electronic effects in the molecule lead to large shifts. A spectrum of a molecule may have a hundred or more absorption bands present, but there is no need to assign the vast majority. The spectrum can be regarded as a 'fingerprint' of the molecule and so this region is referred to as the *fingerprint region*.

3.2.2 Near-Infrared Region

The absorptions observed in the near-infrared region (13 000–4000 cm^{-1}) are overtones or combinations of the fundamental stretching bands which occur in the 3000–1700 cm^{-1} region [1]. The bands involved are usually due to C–H, N–H or O–H stretching. The resulting bands in the near infrared are usually weak in intensity and the intensity generally decreases by a factor of 10 from one overtone to the next. The bands in the near infrared are often overlapped, making them less useful than the mid-infrared region for qualitative analysis. However, there are important differences between the near-infrared positions

of different functional groups and these differences can often be exploited for quantitative analysis.

3.2.3 Far-Infrared Region

The far-infrared region is defined as the region between 400 and 100 cm^{-1} [2]. This region is more limited than the mid infrared for spectra–structure correlations, but does provide information regarding the vibrations of molecules containing heavy atoms, molecular skeleton vibrations, molecular torsions and crystal lattice vibrations. Intramolecular stretching modes involving heavy atoms can be helpful for characterizing compounds containing halogen atoms, organometallic compounds and inorganic compounds. Skeletal bending modes involving an entire molecule occur in the far infrared for molecules containing heavier atoms because bending modes are usually no more than one-half of the wavenumber of the corresponding stretching mode. Torsional modes arise because the rotation about single bonds is not 'free'. As a result, when certain small groups are bonded to a large group, they undergo a motion with respect to the heavier 'anchor' group. Crystal lattice vibrations are associated with the movement of whole molecular chains with respect to each other in crystalline solids.

3.3 Identification

There are a few general rules that can be used when using a mid-infrared spectrum for the determination of a molecular structure. The following is a suggested strategy for spectrum interpretation:

1. Look first at the high-wavenumber end of the spectrum (>1500 cm^{-1}) and concentrate initially on the major bands.
2. For each band, 'short-list' the possibilities by using a correlation chart.
3. Use the lower-wavenumber end of the spectrum for the confirmation or elaboration of possible structural elements.
4. Do not expect to be able to assign every band in the spectrum.
5. Keep 'cross-checking' wherever possible. For example, an aldehyde should absorb near 1730 cm^{-1} and in the region 2900–2700 cm^{-1} (see Chapter 4 for such band assignments).
6. Exploit negative evidence as well as positive evidence. For example, if there is no band in the 1850–1600 cm^{-1} region, it is most unlikely that a carbonyl group is present.
7. Band intensities should be treated with some caution. Under certain circumstances, they may vary considerably for the same group.

8. Take care when using small wavenumber changes. These can be influenced by whether the spectrum was run as a solid or liquid, or in solution. If in solution, some bands are very 'solvent-sensitive'.
9. Do not forget to subtract solvent bands if possible – these could be confused with bands from the sample.

It is not always possible by examination of the infrared spectrum of a compound alone to identify it unequivocally. It is normal to use infrared spectroscopy in conjunction with other techniques, such as chromatographic methods, mass spectrometry, NMR spectroscopy and various other spectroscopic techniques.

Advances in computer retrieval techniques have extended the range of information available from an infrared instrument by allowing comparison of an unknown spectrum with a 'bank' of known compounds. This was only possible in the past by manually searching libraries of spectra. Once the compound was classified, the atlas of spectra could be searched for an identical or very similar spectrum. Computers have accelerated this search process. The programs work by hunting through stored data to match intensities and wavenumbers of absorption bands [3]. The computer will then output the best fits and the names of the compounds found.

3.4 Hydrogen Bonding

The presence of hydrogen bonding is of great importance in a range of molecules. For instance, the biological activity of deoxyribonucleic acid (DNA) relies on this type of bonding. Hydrogen bonding is defined as the attraction that occurs between a highly electronegative atom carrying a non-bonded electron pair (such as fluorine, oxygen or nitrogen) and a hydrogen atom, itself bonded to a small highly electronegative atom. An example of this type of bonding is illustrated by the interactions between water molecules in Figure 3.1. This is an example of *intermolecular* hydrogen bonding. It is also possible for a hydrogen bond to form between appropriate groups within the one molecule. This is known as *intramolecular* hydrogen bonding and is illustrated by the protein structure shown in Figure 3.2. The segments shown belong to the same protein molecule.

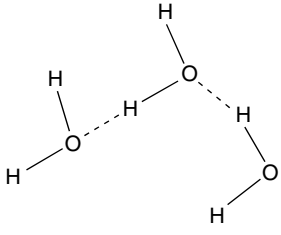

Figure 3.1 Hydrogen bonding of water molecules.

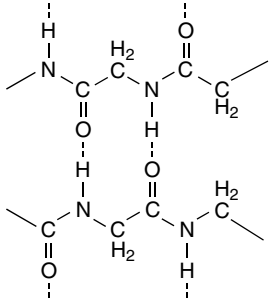

Figure 3.2 Intramolecular hydrogen bonding in a protein.

DQ 3.1

Would chloroform be expected to form hydrogen bonds? If so, would those bonds be intramolecular or intermolecular?

Answer

Chloroform ($CHCl_3$) possesses a donor hydrogen but no suitable lone pair exists in the molecule to form a strong hydrogen bond. A very weak hydrogen bond could form with the chlorine lone pairs. Thus, this is a marginal case of intermolecular hydrogen bonding.

SAQ 3.1

Would the O–H stretching mode be expected to vary in intensity when hydrogen bonded. If so, would it decrease or increase?

Hydrogen bonding is a very important effect in infrared spectroscopy. This bonding influences the bond stiffness and so alters the frequency of vibration. For example, for a hydrogen bond in an alcohol, the O–H stretching vibration in a hydrogen-bonded dimer is observed in the 3500–2500 cm^{-1} range, rather than in the usual 3700–3600 cm^{-1} range (Figure 3.3).

Many solvents are capable of forming hydrogen bonds to solutes. Three classes of solvent exist which may lead to trouble when used for hydrogen-bonding

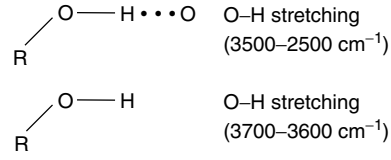

Figure 3.3 Effect of hydrogen bonding on an O–H stretching vibration.

studies is solution. First, compounds which contain hydrogen donor groups, e.g. halogenated compounds which contain a sufficient number of halogens to activate the hydrogens present, such as chloroform. Secondly, compounds which contain non-bonded electron pairs, such as ethers, aldehydes and tertiary amines. In addition, there are compounds which contain both types of group, e.g. water and alcohols. There are only a few solvents that do not have the above characteristics, such as carbon tetrachloride (CCl_4) and carbon disulfide (CS_2). These still contain lone electron pairs, but being on S and Cl are less available, and any interactions will be extremely weak.

Apart from solvent effects, concentration and temperature also affect the degree of hydrogen bonding in a compound. The lower the concentration, then the less chance there is of two molecules colliding. It follows that the degree of hydrogen bonding decreases with decreasing concentration.

DQ 3.2

What would be the effect of an increase in temperature on the infrared spectrum of a hydrogen-bonded compound?

Answer

Increasing temperature means that each molecule will have more energy on average and weak associative forces, such as hydrogen bonds, are likely to be broken. This should lead to a lesser degree of hydrogen bonding, and thus changes in wavenumber to greater values would be observed for groups forming the hydrogen bond.

3.5 Spectrum Manipulation

There are a number of techniques available to users of infrared spectrometers that help with both the qualitative and quantitative interpretation of spectra.

3.5.1 Baseline Correction

It is usual in quantitative infrared spectroscopy to use a baseline joining the points of lowest absorbance on a peak, preferably in reproducibly flat parts of the absorption line. The absorbance difference between the baseline and the top of the band is then used. An example of a baseline construction is shown in Figure 3.4.

3.5.2 Smoothing

'Noise' in a spectrum can be diminished by a smoothing process. After a spectrum is smoothed, it becomes similar to the result of an experiment at a lower

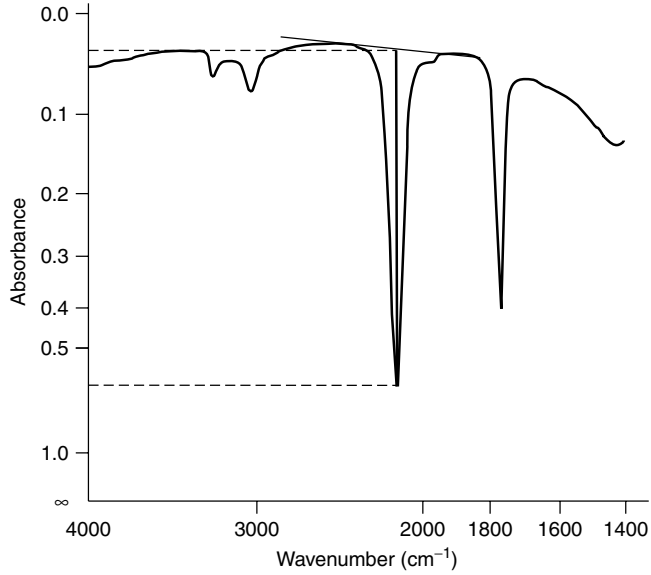

Figure 3.4 An example of a baseline correction. From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

resolution. The features are blended into each other and the noise level decreases. A smoothing function is basically a convolution between the spectrum and a vector whose points are determined by the degree of smoothing applied. Generally, a degradation factor is required, which will be some positive integer. A low value, say one, will produce only subtle changes, while a high value has a more pronounced effect on the spectrum.

3.5.3 Difference Spectra

The most straightforward method of analysis for complex spectra is *difference spectroscopy*. This technique may be carried out by simply subtracting the infrared spectrum of one component of the system from the combined spectrum to leave the spectrum of the other component. If the interaction between components results in a change in the spectral properties of either one or both of the components, the changes will be observed in the difference spectra. Such changes may manifest themselves via the appearance of positive or negative peaks in the spectrum.

Spectral subtraction may be applied to numerous applications and can be used for the data collected for solutions. In order to obtain the spectrum of a solution, it is necessary to record spectra of both the solution and the solvent alone. The solvent spectrum may then be subtracted from the solution spectrum. Figure 3.5,

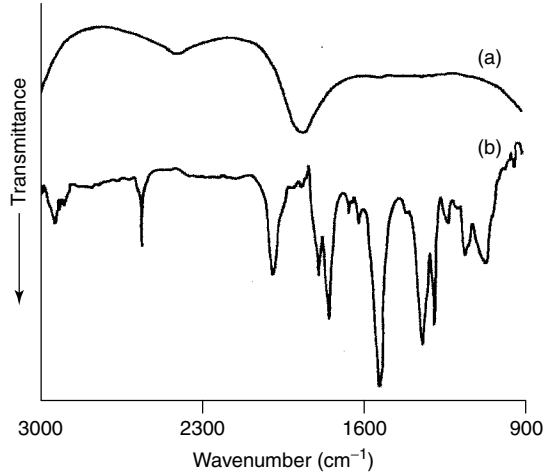

Figure 3.5 Infrared spectra of (a) a 1% (wt/vol) solution of aspirin in water and (b) the same solution after subtraction of the water spectrum. From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

where the strong infrared spectrum of water has been removed from a relatively weak spectrum of a 1% (wt/vol) solution of aspirin, illustrates how subtraction can be very useful in FTIR spectroscopy. However, care must be exercised because the concentration of the solvent alone is greater than that of the solvent in the solution and negative peaks may appear in the regions of solvent absorption.

Under certain circumstances, the spectrum due to the solvent may be very intense, making simple subtraction impossible. This situation can make it difficult to investigate the sample spectrum, as solvent bands may overlap with the region under investigation. In such experiments, attenuated total reflectance (ATR) spectroscopy provides a suitable approach. The nature of the ATR technique produces a less intense solvent contribution to the overall infrared spectrum and so solvent spectra can be more readily subtracted from the sample spectrum of interest by using this method.

Subtraction may also be applied to solid samples and is especially useful for mulls. The spectrum of the mulling agent can be subtracted, hence giving the spectrum of the solid only.

3.5.4 Derivatives

Spectra may also be differentiated. Figure 3.6 shows a single absorption peak and its first and second derivative. The benefits of derivative techniques are twofold. Resolution is enhanced in the first derivative since changes in the gradient are examined. The second derivative gives a negative peak for each band and shoulder in the absorption spectrum.

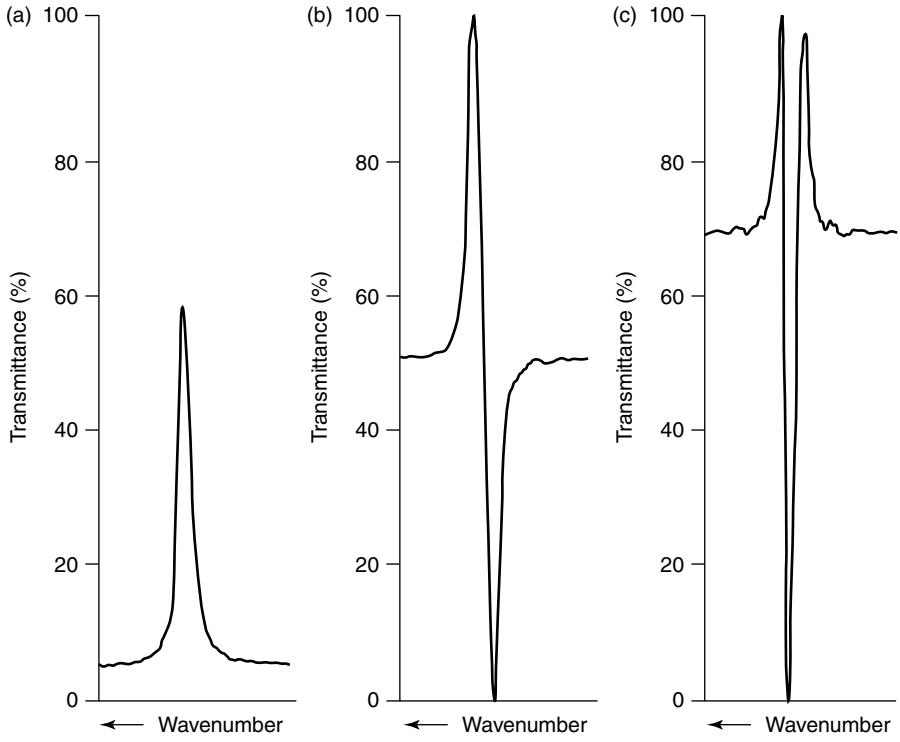

Figure 3.6 Differentiation of spectra: (a) single absorption peak; (b) first derivative; (c) second derivative. From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

The advantage of derivatization is more readily appreciated for more complex spectra and Figure 3.7 shows how differentiation may be used to resolve and locate peaks in an 'envelope'. Note that sharp bands are enhanced at the expense of broad ones and this may allow for the selection of a suitable peak, even when there is a broad band beneath.

With FTIR spectrometers, it is possible to apply what is known as *Fourier-derivation*. During this process, the spectrum is first transformed into an interferogram. It is then multiplied by an appropriate weighting function and finally it is 're-transformed' to give the derivative. This technique provides more sensitivity than conventional derivatization.

3.5.5 Deconvolution

Deconvolution is the process of compensating for the intrinsic linewidths of bands in order to resolve overlapping bands [4]. This technique yields spectra that have

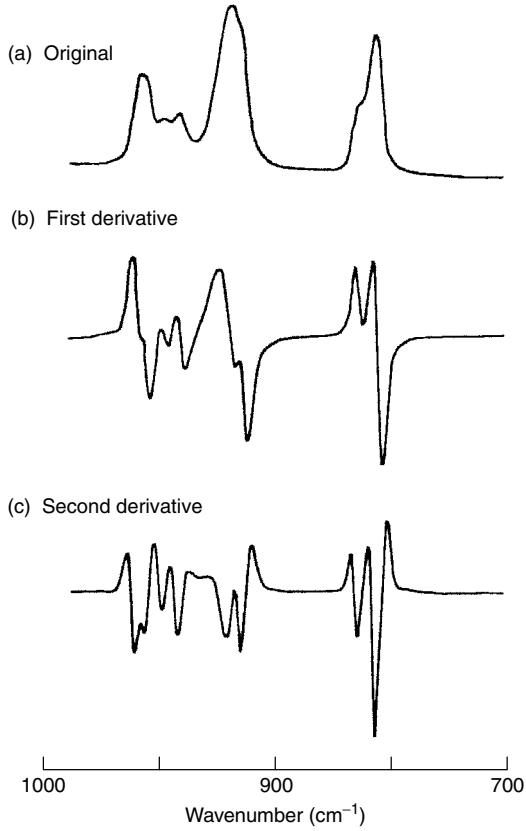

Figure 3.7 Complex absorption band (a), plus corresponding first (b) and second (c) derivatives. From *Perkin-Elmer Application Notes on Derivative Spectroscopy*, Perkin-Elmer, Norwalk, CT, USA, 1984, and reproduced with permission of the Perkin-Elmer Corporation.

much narrower bands and is able to distinguish closely spaced features. The instrumental resolution is not increased, but the ability to differentiate spectral features can be significantly improved. This is illustrated by Figure 3.8, which shows a broad band before and after deconvolution has been applied. The peaks at quite close wavenumbers are now easily distinguished.

The deconvolution technique generally involves several steps: computation of an interferogram of the sample by computing the inverse Fourier-transform of the spectrum, multiplication of the interferogram by a smoothing function and by a function consisting of a Gaussian–Lorentzian bandshape, and Fourier-transformation of the modified interferogram.

The deconvolution procedure is typically repeated iteratively for best results. At iteration, the lineshape is adjusted in an attempt to provide narrower bands

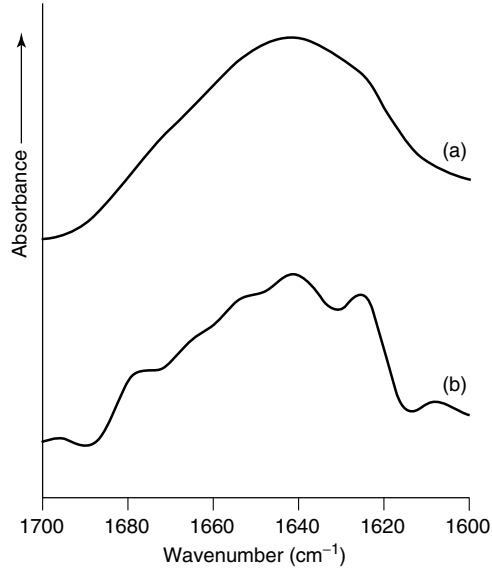

Figure 3.8 Broad infrared band (a) before and (b) after deconvolution. From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

without excessive distortion. There are three parameters that can be adjusted to 'tune' the lineshape, as follows. First, the proportion of Gaussian and Lorentzian lineshapes: the scale of these components is adjusted depending on the predicted origins of the bandshape. For instance, it will vary depending on whether a solid, liquid or gas is being investigated. The second factor is the half-width: this is the width of the lineshape. The half-width is normally the same as or larger than the intrinsic linewidth (full-width at half-height) of the band. If the value specified is too small, then the spectrum tends to show only small variations in intensity. If too large, distinctive negative side-lobes are produced. The narrowing function is a further factor: this is the degree of narrowing attempted on a scale from 0 to 1. If the narrowing function is specified too small, then the resulting spectrum will not be significantly different from the original, while if too large, the spectrum may produce false peaks as noise starts to be deconvolved.

3.5.6 Curve-Fitting

Quantitative values for band areas of heavily overlapped bands can be achieved by using curve-fitting procedures. Many of these are based on a least-squares minimization procedure. Least-squares curve-fitting covers the general class of techniques whereby one attempts to minimize the sum of the squares of the difference between an experimental spectrum and a computed spectrum generated by

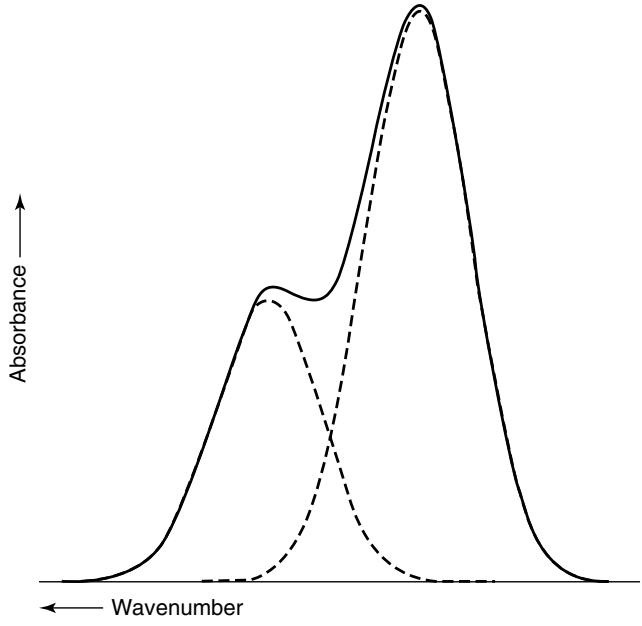

Figure 3.9 Illustration of curve-fitting of overlapping infrared bands.

summing the component curves. Generally, the procedure involves entering the values of the wavenumbers of the component bands (determined by using derivatives and/or deconvolution) and then the program determines the best estimate of the parameters of the component curves.

Apart from the obvious variables of peak height and width, the type of bandshape needs to be considered. The class of bandshape of an infrared spectrum depends on the type of sample. A choice of Gaussian, Lorentzian or a combination of these band shapes is usually applied. Figure 3.9 illustrates the results of a curve-fitting process.

3.6 Concentration

The Beer–Lambert law is used to relate the amount of light transmitted by a sample to the thickness of the sample. The *absorbance* of a solution is directly proportional to the thickness and the concentration of the sample, as follows:

$$A = \varepsilon cl \tag{3.1}$$

where A is the absorbance of the solution, c the concentration and l the pathlength of the sample. The constant of proportionality is usually given the Greek symbol epsilon, ε, and is referred to as the *molar absorptivity*.

The absorbance is equal to the difference between the logarithms of the intensity of the light entering the sample (I_0) and the intensity of the light transmitted (I) by the sample:

$$A = \log\ I_0 - \log I = \log\ (I_0/I) \tag{3.2}$$

Absorbance is therefore dimensionless. *Transmittance* is defined as follows:

$$T = I/I_0 \tag{3.3}$$

and percentage transmittance as:

$$\%T = 100 \times T \tag{3.4}$$

Thus:

$$A = -\log\ (I/I_0) = -\log T \tag{3.5}$$

When using percentage transmittance values, it is easy to relate and to understand the numbers. For example, 50% transmittance means that half of the light is transmitted and half is absorbed, while 75% transmittance means that three quarters of the light is transmitted and one quarter absorbed.

DQ 3.3

What would be the absorbance of a solution that has a percentage transmittance of: (a) 100%; (b) 50%; (c) 10%; (d) 0%?

Answer

The use of Equations (3.4) and (3.5) gives:

(a) A = *−log (100/100) = 0;*

(b) A = *−log (50/100) = 0.303;*

(c) A = *−log (10/100) = 1.0;*

(d) A = *−log (0/100) = infinity.*

The important point to gain from these figures is that at an absorbance of 1.0, 90% of the light is being absorbed, and so the instrument's detector does not have much radiation with which to work.

SAQ 3.2

A 1.0% (wt/vol) solution of hexanol has an infrared absorbance of 0.37 at 3660 cm^{-1} in a 1.0 mm cell. Calculate its molar absorptivity at this wavenumber.

The Beer–Lambert law tells us that a plot of absorbance against concentration should be linear with a gradient of εl and will pass through the origin. In theory, to analyse a solution of unknown concentration, solutions of known concentration need to be prepared, a suitable band chosen, the absorbance at this wavenumber measured, and a calibration graph plotted. The concentration o the compound in solution can be read from the calibration graph, given that its absorbance is known.

There are a few factors which need to be considered when taking this approach. First, the preparation of solutions of known concentrations: these concentrations have to give sensible absorbance values – not too weak and not too intense. There is also the choice of a suitable absorption peak: this technique needs to be as sensitive as possible and so an intense peak should be chosen. However, often infrared spectra have many, sometimes overlapping peaks. A peak isolated from others, with a high molar absorptivity, should be found. A further problem that sometimes arises, especially in the spectra of solid samples, is the presence of asymmetric bands. In such cases, peak height cannot be used because the baseline will vary from sample to sample and peak area measurements must be used instead. FTIR spectrometers have accompanying software that can carry out these calculations (calibration methods are introduced below in Section 3.9). Quantitative measurements need to be carried out on absorbance spectra. Thus, transmittance spectra need to be converted to absorbance spectra.

The determination of the concentration of a gas needs to be considered separately from solids and liquids [5]. The ideal gas law relates the physical properties of a gas to its concentration. This law states that:

$$PV = nRT \tag{3.6}$$

where P is the pressure, V the volume, n the number of moles, R the universal gas constant and T the temperature. Given that the concentration of a gas in an infrared cell is given by $c = n/V$, Equation (3.1) may be rewritten as follows:

$$A = P\varepsilon l/RT \tag{3.7}$$

Thus, for gases the absorbance depends also upon the pressure and the temperature of the gas.

3.7 Simple Quantitative Analysis

3.7.1 Analysis of Liquid Samples

The quantitative analysis of a component in solution can be successfully carried out given that there is a suitable band in the spectrum of the component of interest. The band chosen for analysis should have a high molar absorptivity, not overlap with other peaks from other components in the mixture or the solvent, be symmetrical, and give a linear calibration plot of absorbance versus concentration.

Most simple quantitative infrared methods of analysis use the intensities of the C=O, N–H or O–H groups. The C=O stretching band is the most commonly used because it is a strong band in a spectral region relatively free of absorption by other functional groups. In addition, the carbonyl band is not as susceptible as the O–H and N–H bands to chemical change or hydrogen bonding.

Simple quantitative analysis can be illustrated by using the example of aspirin dissolved in chloroform. The best peak to choose in this example is the C=O stretching band of aspirin, observed at 1764 cm^{-1}, because it is an intense peak and

Table 3.1 Calibration data for aspirin solutions. From Stuart, B., *Biological Applications of Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1997. © University of Greenwich, and reproduced by permission of the University of Greenwich

Concentration (mg ml^{-1})	Absorbance at 1764 cm^{-1}
0	0.000
25	0.158
50	0.285
75	0.398
100	0.501

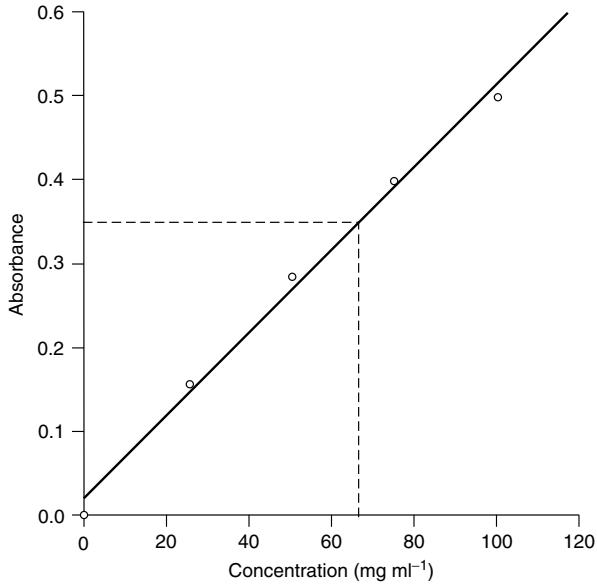

Figure 3.10 Calibration graph for aspirin solutions. From Stuart, B., *Biological Applications of Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1997. © University of Greenwich, and reproduced by permission of the University of Greenwich.

lies in a region where there is no interference from the chloroform spectrum. The next step is to draw a calibration plot of absorbance versus aspirin concentration. A series of chloroform solutions of known aspirin concentrations is prepared and the infrared spectrum of each solution recorded by using a 0.1 mm NaCl transmission cell. The absorbance of the 1764 cm^{-1} band is measured for each solution, with the results obtained being listed in Table 3.1. These data can then be graphed to produce a linear plot, as shown in Figure 3.10. The next stage in the analysis is to determine the amount of aspirin present in a chloroform solution of unknown concentration. The infrared spectrum of the unknown sample is recorded and the absorbance of the 1764 cm^{-1} carbonyl band was measured as 0.351. Using the calibration graph, this corresponds to a concentration of 67 mg ml^{-1}.

SAQ 3.3

A solution of caffeine in chloroform is provided for analysis, with the concentration of caffeine in the solution being required. Caffeine in chloroform shows a distinct carbonyl band at 1656 cm^{-1} in the infrared spectrum (recorded by using a 0.1 mm NaCl cell). The infrared information provided by standard solutions of caffeine in chloroform is listed below in Table 3.2. Given that the unknown sample produces an absorbance of 0.166 at 1656 cm^{-1} in its infrared spectrum, determine the concentration of this caffeine sample. Assume that there is no interference from other components in the sample.

Table 3.2 Calibration data for caffeine solutions (cf. SAQ 3.3). From Stuart, B., *Biological Applications of Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1997. © University of Greenwich, and reproduced by permission of the University of Greenwich

Concentration (mg ml^{-1})	Absorbance at 1656 cm^{-1}
0	0.000
5	0.105
10	0.190
15	0.265
20	0.333

SAQ 3.4

Commercial propanol often contains traces of acetone formed by oxidation. Acetone shows a distinct band at 1719 cm^{-1} suitable for quantitative analysis. The absorbance values at 1719 cm^{-1} versus the concentrations of a series of prepared solutions containing known quantities of acetone are listed below in Table 3.3.

The density of acetone is 0.790 g cm^{-3} and the pathlength used was 0.1 mm. The infrared spectrum of a 10 vol% solution of commercial propanol in CCl_4 in a 0.1 mm pathlength cell was recorded and a band of absorbance 0.337 at 1719 cm^{-1} is observed in the spectrum. Determine the concentration (in mol l^{-1}) of acetone in this solution and calculate the percentage acetone in the propanol.

Table 3.3 Calibration data for solutions of acetone in propanol (cf. SAQ 3.4). From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich

Acetone in CCl_4 (vol%)	Absorbance at 1719 cm^{-1}
0.25	0.123
0.50	0.225
1.00	0.510
1.50	0.736
2.00	0.940

Infrared spectroscopy can be used to measure the number of functional groups in a molecule, for example, the number of –OH or $–NH_2$ groups. It has been found that the molar absorptivities of the bands corresponding to the group are proportional to the number of groups that are present, that is, each group has its own intensity which does not vary drastically from molecule to molecule. This approach has been used to measure chain lengths in hydrocarbons by using the C–H deformation, the methylene group at 1467 and 1305 cm^{-1}, and the number of methyl groups in polyethylene.

3.7.2 Analysis of Solid Samples

Simple solid mixtures may also be quantitatively analysed. These are more susceptible to errors because of the scattering of radiation. Such analyses are usually carried out with KBr discs or in mulls. The problem here is the difficulty in measuring the pathlength. However, this measurement becomes unnecessary when an internal standard is used. When using this approach, addition of a constant known amount of an internal standard is made to all samples and calibration standards. The calibration curve is then obtained by plotting the ratio of the absorbance of the analyte to that of the internal standard, against the concentration of the analyte. The absorbance of the internal standard varies linearly with the sample thickness and thus compensates for this parameter. The discs or mulls must be prepared under exactly the same conditions to avoid intensity changes or shifts in band positions.

The standard must be carefully chosen and it should ideally possess the following properties: have a simple spectrum with very few bands; be stable to heat and not absorb moisture; be easily reduced to a particle size less than the incident radiation without lattice deformation; be non-toxic, giving clear discs in a short time; be readily available in the pure state. Some common standards used include calcium carbonate, sodium azide, napthalene and lead thiocyanate.

3.8 Multi-Component Analysis

The analysis of a component in a complex mixture presents special problems. In this section, the approach to determining the concentrations of a number of components in a mixture will be examined. The simple approach taken here serves to illustrate the fundamental ideas of analysis of mixtures, while the mathematical methods that may be employed to analyse multicomponent infrared data are summarized below in Section 3.9.

The quantitative analysis of a multi-component system is illustrated by its application to the simultaneous determination of a mixture of xylene isomers. Commercial xylene is a mixture of isomers, i.e. 1,2-dimethylbenzene (*o*-xylene), 1,3-dimethylbenzene (*m*-xylene) and 1,4-dimethylbenzene (*p*-xylene). The

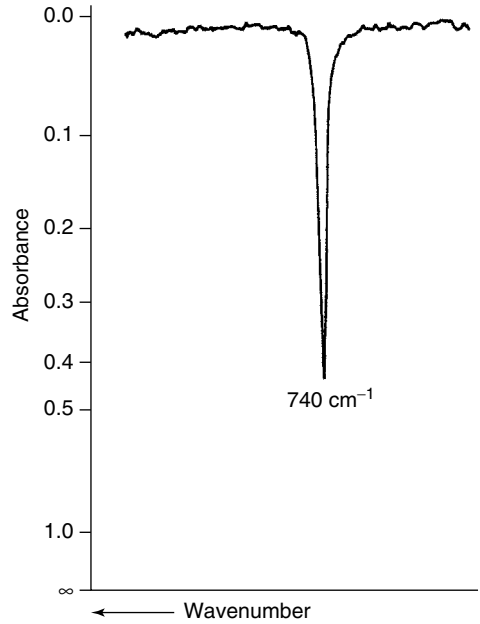

Figure 3.11 Infrared spectrum of *o*-xylene in cyclohexane (1 vol%, 0.1 mm pathlength). From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

spectra of these three *pure* xylenes in cyclohexane solutions (Figures 3.11, 3.12 and 3.13) all show strong bands in the 800–600 cm^{-1} region. Cyclohexane has a very low absorbance in this region and is therefore a suitable solvent for the analysis. The infrared spectrum of a commercial sample of xylene is given in Figure 3.14.

The concentration of the three isomers may be estimated in the commercial sample. First, the absorbances of the xylenes at 740, 770 and 800 cm^{-1} from the standards shown in Figures 3.11, 3.12 and 3.13 need to be measured, as follows:

$$o\text{-xylene} \quad 740\ cm^{-1} \quad A = 0.440 - 0.012 = 0.428$$

$$m\text{-xylene} \quad 770\ cm^{-1} \quad A = \frac{0.460 - 0.015}{2} = 0.223$$

$$p\text{-xylene} \quad 800\ cm^{-1} \quad A = \frac{0.545 - 0.015}{2} = 0.265$$

The values for *m*-xylene and *p*-xylene are divided by two as these solutions are twice as concentrated. The absorbance values have also been corrected for a non-zero baseline in the region. The absorbance values are proportional to the molar

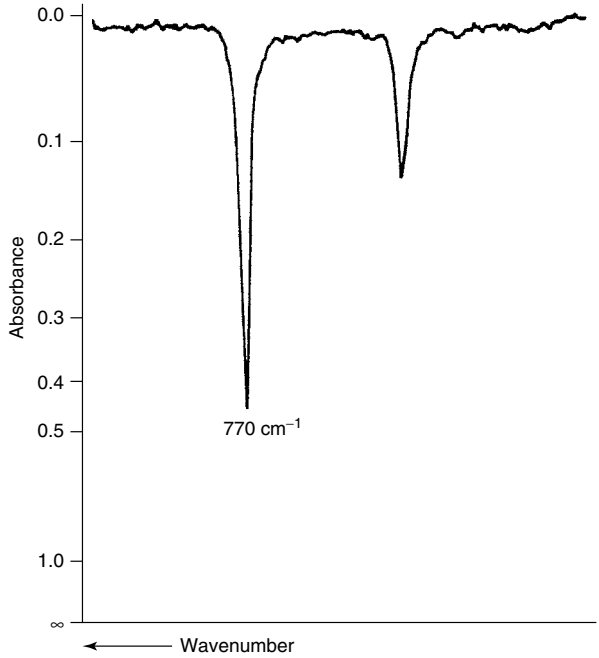

Figure 3.12 Infrared spectrum of *m*-xylene in cyclohexane (2 vol%, 0.1 mm pathlength). From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

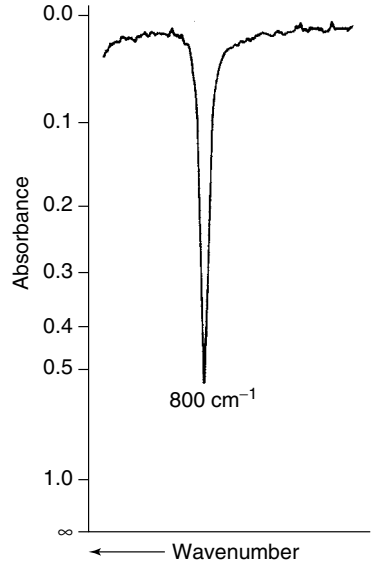

Figure 3.13 Infrared spectrum of *p*-xylene in cyclohexane (2 vol%, 0.1 mm pathlength). From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

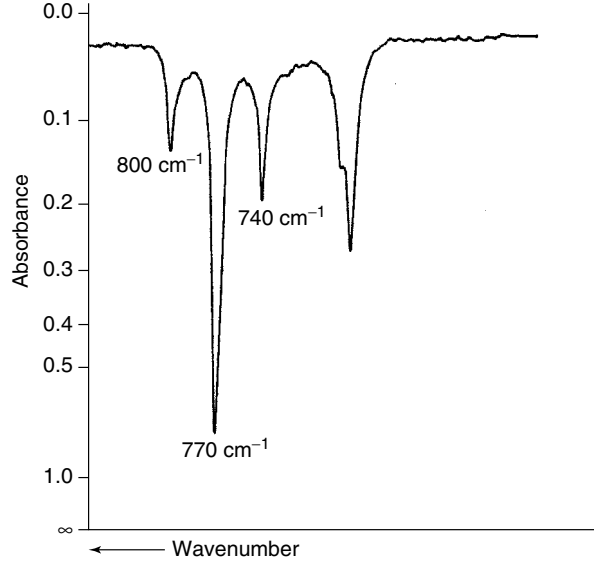

Figure 3.14 Infrared spectrum of commercial xylene in cyclohexane (5 vol%, 0.1 mm pathlength). From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

absorptivities, and hence the concentrations of the xylenes can be estimated in the mixture once the absorbances are measured. From Figure 3.14, we obtain:

$$740\ \text{cm}^{-1} \quad A = 0.194 - 0.038 = 0.156$$
$$770\ \text{cm}^{-1} \quad A = 0.720 - 0.034 = 0.686$$
$$800\ \text{cm}^{-1} \quad A = 0.133 - 0.030 = 0.103$$

Dividing these absorbance values by the standard values, gives the vol% of each isomer in the mixture:

$$o\text{-xylene} = 0.156/0.428 = 0.364\ \text{vol\%}$$
$$m\text{-xylene} = 0.686/0.223 = 3.076\ \text{vol\%}$$
$$p\text{-xylene} = 0.103/0.265 = 0.389\ \text{vol\%}$$

It should be pointed out that there are potential sources of error in these values. There can be error due to the fact that it is difficult to select a baseline for the analysis because of overlapping peaks. In addition, any non-linearity of the Beer–Lambert law plots has been ignored, having used one value to determine the constant of proportionality above for each solution. Alternatively, this same problem for xylene can be determined by spectral subtraction. If a sample of the impurity is available, mixtures of the starting material and product can be separated by subtraction of the spectra of the mixture and impurities. This is achieved by subtracting a fraction of *o*-xylene, then *m*-xylene and finally *p*-xylene from the commercial xylene spectrum to 'null' the corresponding absorptions.

Table 3.4 Calibration data for a drug mixture (cf. SAQ 3.5). From Stuart, B., *Biological Applications of Infrared spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1997. © University of Greenwich, and reproduced by permission of the University of Greenwich

Component	Concentration (mg ml^{-1})	C=O stretching wavenumber (cm^{-1})	Absorbance
Aspirin	90	1764	0.217
Phenacetin	65	1511	0.185
Caffeine	15	1656	0.123

SAQ 3.5

Quantitative analysis of tablets containing aspirin, phenacetin and caffeine is to be carried out. Each of these components show distinct carbonyl bands in chloroform solution and calibration data for known concentrations are listed below in Table 3.4. Each of the standards was studied by using a 0.1 mm pathlength

NaCl transmission cell. Given that the absorbance values for an unknown tablet produced under the same conditions are given below in Table 3.5, estimate the concentrations of aspirin, phenacetin and caffeine in the unknown tablet.

Table 3.5 Absorbance values for an unknown drug mixture (cf. SAQ 3.5). From Stuart, B., *Biological Applications of Infrared spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1997. © University of Greenwich, and reproduced by permission of the University of Greenwich

Wavenumber (cm^{-1})	Absorbance
1764	0.207
1511	0.202
1656	0.180

3.9 Calibration Methods

The improvement in computer technology associated with spectroscopy has led to the expansion of quantitative infrared spectroscopy. The application of statistical methods to the analysis of experimental data is known as *chemometrics* [5–9]. A detailed description of this subject is beyond the scope of this present text, although several multivariate data analytical methods which are used for the analysis of FTIR spectroscopic data will be outlined here, without detailing the mathematics associated with these methods. The most commonly used analytical methods in infrared spectroscopy are classical least-squares (CLS), inverse least-squares (ILS), partial least-squares (PLS), and principal component regression (PCR). CLS (also known as K-matrix methods) and PLS (also known as P-matrix methods) are least-squares methods involving matrix operations. These methods can be limited when very complex mixtures are investigated and factor analysis methods, such as PLS and PCR, can be more useful. The factor analysis methods use functions to model the variance in a data set.

If it is not necessary to know the specific concentrations of the species of interest, but to simply know whether such species are present, or not, in a complex sample; then, a multivariate pattern recognition method, such as linear discriminant analysis (LDA) or artificial neural networks (ANNs), may be used to identify the spectral characteristics of the species of interest [10]. Such methods are capable of comparing a large number of variables within a data set, such as intensity, frequency and bandwidth. LDA and ANNs are known as *supervised* methods because *a priori*

information is available about the data sets. There are also *unsupervised* methods, such as hierarchical clustering, which can be used to determine the components in a data set without any prior information about the data.

The use of calibration methods in infrared spectroscopy is illustrated here by an example of the application of PCR to the analysis of vegetable oils [11]. Figure 3.15 shows the superposition of the infrared spectra of five different types of vegetable oil. This demonstrates the similarity of these spectra and the difficulty in differentiating the samples by simple inspection. However, there are characteristic differences in the band positions of each spectrum which may be exploited by using PCR; the wavenumbers of the C–H stretching and C–H bending bands and bands in the fingerprint region can be used as variables. The process of analysis involves a series of steps. Replicate spectra should first be obtained for the oils to be analysed and for the unknown samples. The mean of each wavenumber for each class of oil should be calculated. The absolute difference between the unknown wavenumber and the means for each class and each band are then determined. Then, the sum of the differences for each class across all bands employed is determined and the assignment of the unknown to the class with the smallest sum of differences can be made. The results of the analysis of a mixture of unknown vegetable oils, with seven peaks being used, are shown in Figure 3.16. Different symbols are used here to represent each type of

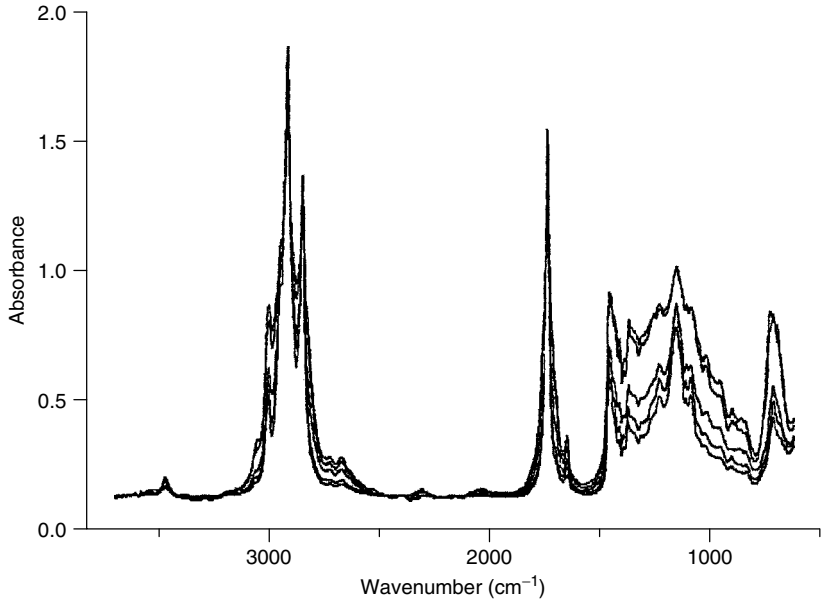

Figure 3.15 Infrared spectra of a mixture of five different vegetable oils [11]. Used with permission from the *Journal of Chemical Education*, **80**, No. 5, 2003, pp. 541–543; Copyright ©2003, Division of Chemical Education, Inc.

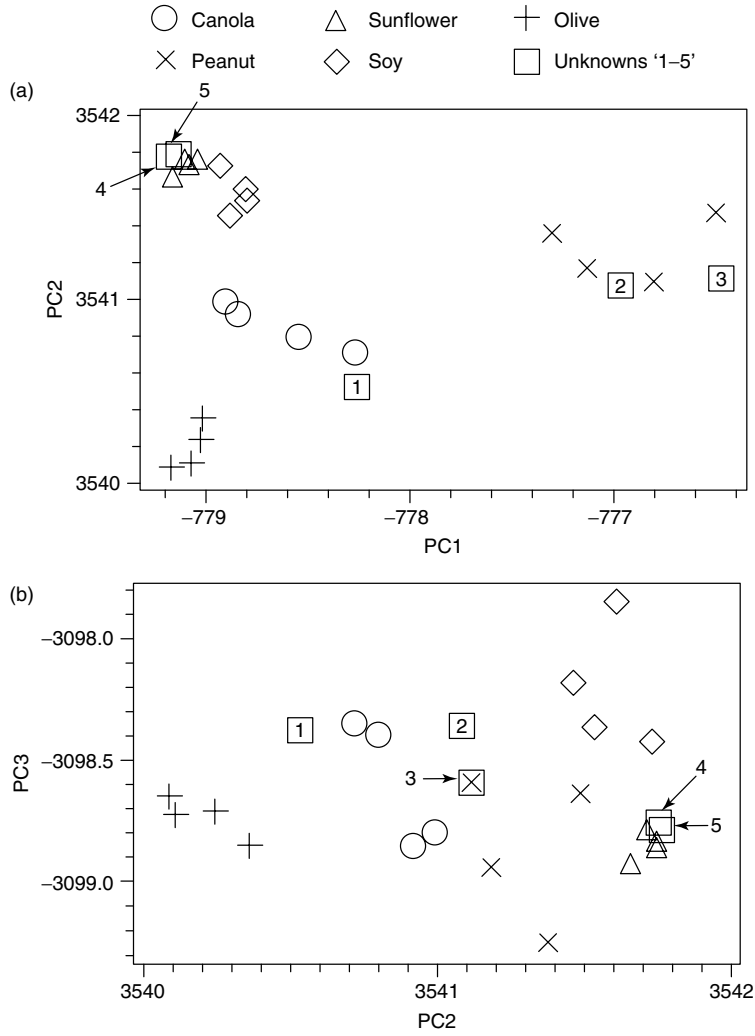

Figure 3.16 Plots of the principal component scores for vegetable oil analysis [11]. Used with permission from the *Journal of Chemical Education*, **80**, No. 5, 2003, pp. 541–543; Copyright ©2003, Division of Chemical Education, Inc.

known oil and each unknown oil. The plot illustrated in Figure 3.16(a) shows a PC2 versus PC1 plot and indicates that olive, canola and peanut oils form distinct clusters. This plot can be used to assign unknown '1' to the canola group and unknowns '2' and '3' to the peanut group. The plot illustrated in Figure 3.16(b) shows a PC3 versus PC2 plot. While sunflower and soy oil were not distinguishable in the PC2 versus PC1 plot, they are well separated in the PC3 versus PC2

plot. Unknowns '4' and '5' can be identified as sunflower oil because of their clustering near the sunflower oil 'knowns' in both plots.

Summary

In this chapter, the issues associated with both the qualitative and quantitative analysis of infrared spectra were described. The mid-, near- and far-infrared regions of a spectrum were introduced and the bands in these regions were assigned to particular types of molecular vibrations. Hydrogen bonding, a factor that influences infrared bands, was discussed in this chapter. An approach to the qualitative analysis of spectra was also described.

The various ways in which a spectrum can be manipulated in order to carry out quantitative analysis were examined. These included baseline correction, smoothing, derivatives, deconvolution and curve-fitting. The Beer–Lambert law was also introduced, showing how the intensity of an infrared band is related to the amount of analyte present. This was then applied to the simple analysis of liquid and solid samples. Then followed a treatment of multi-component mixtures. An introduction to the calibration methods used by infrared spectroscopists was also provided.

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Chapter 4
Organic Molecules

Learning Objectives

- To assign the infrared bands of the main classes of organic molecules.
- To identify the structures of organic molecules by using the infrared spectra of such molecules.

4.1 Introduction

One of the most common applications of infrared spectroscopy is to the identification of organic compounds. The major classes of organic molecules are examined in turn in this chapter and useful group frequencies are detailed. There are a number of useful collections of spectral information regarding organic molecules that may be used for reference and combined with the information provided in this chapter [1–7]. A series of questions are also provided to practice the assignment of bands observed in organic infrared spectra and to use the spectra to characterize the structures of organic molecules.

4.2 Aliphatic Hydrocarbons

Alkanes contain only C–H and C–C bonds, but there is plenty of information to be obtained from the infrared spectra of these molecules. The most useful are those arising from C–H stretching and C–H bending. C–H stretching bands in aliphatic

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hydrocarbons appear in the 3000–2800 cm^{-1} range and the C–H stretching bands of methyl groups and methylene groups are readily differentiated. For methyl groups, asymmetric C–H stretching occurs at 2870 cm^{-1}, while symmetric C–H stretching occurs at 2960 cm^{-1}. By comparison, methylene groups show asymmetric stretching at 2930 cm^{-1} and symmetric stretching at 2850 cm^{-1}. C–H bending gives rise to bands in the region below 1500 cm^{-1}. Methyl groups produce two bending bands, i.e. a symmetrical band at 1380 cm^{-1} and an asymmetrical band at 1475 cm^{-1}. Methylene groups give rise to four bending vibrations: scissoring (1465 cm^{-1}), rocking (720 cm^{-1}), wagging (1305 cm^{-1}) and twisting (1300 cm^{-1}). The intensity of the methylene CH_2 rocking band is useful as four or more CH_2 groups are required in a chain to produce a distinct band near 720 cm^{-1}. Shorter chains show a more variable band, for instance, the CH_2 rocking band for C_4H_{10} is near 734 cm^{-1}. Although these are the main characteristic bands associated with aliphatic hydrocarbons, there are a number of bands that appear in the spectra of such compounds as there is a wide range of structures possible. The main infrared bands for alkanes are summarized in Table 4.1.

Table 4.1 Characteristic infrared bands of aliphatic hydrocarbons

Wavenumber (cm^{-1})	Assignment
	Alkanes
2960	Methyl symmetric C–H stretching
2930	Methylene asymmetric C–H stretching
2870	Methyl asymmetric C–H stretching
2850	Methylene symmetric C–H stretching
1470	Methyl asymmetrical C–H bending
1465	Methylene scissoring
1380	Methyl symmetrical C–H bending
1305	Methylene wagging
1300	Methylene twisting
720	Methylene rocking
	Alkenes
3100–3000	=C–H stretching
1680–1600	C=C stretching
1400	=C–H in-plane bending
1000–600	=C–H out-of-plane bending
	Alkynes
3300–3250	=C–H stretching
2260–2100	C=C stretching
700–600	=C–H bending

SAQ 4.1

Examine the infrared spectrum of nonane shown below in Figure 4.1 and describe the vibrations corresponding to the bands marked A, B and C.

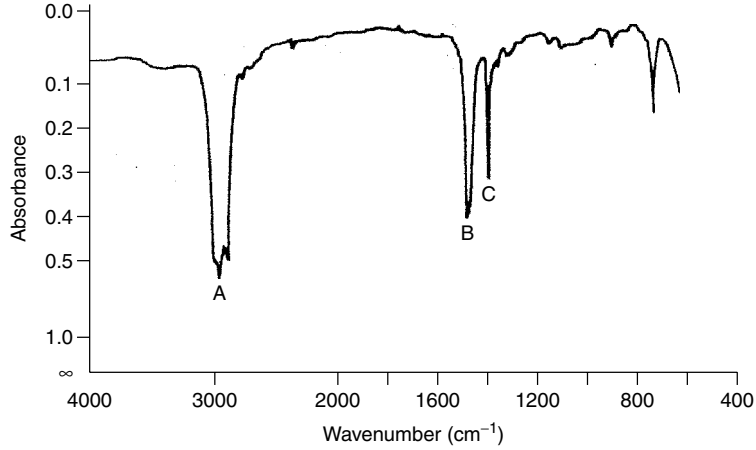

Figure 4.1 Infrared spectrum of nonane (C_9H_{20}) (cf. SAQ 4.1). From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

SAQ 4.2

From the following list of compounds, 2-methylbutane, cyclopentane, 2-methyloctane, 3-methylpentane, butane and 1,1-dimethylcyclohexane, choose those that:

(a) absorb at 720 cm^{-1};
(b) absorb at 1375 cm^{-1};
(c) absorb at both 720 and 1375 cm^{-1};
(d) do not absorb at either 720 or 1375 cm^{-1}.

Alkenes contain the C=C group, with the majority having hydrogen attached to the double bond. Four major bands are associated with this molecular fragment. These are the out-of-plane and in-plane =C–H deformations, C=C stretching and =C–H stretching. The characteristic infrared modes observed for alkenes are given in Table 4.1.

Alkynes contain the C≡C group and three characteristic bands can be present, i.e. ≡C–H stretching, ≡C–H bending and C≡C stretching. The main bands observed for alkynes are also shown in Table 4.1.

Table 4.2 Characteristic infrared bands of aromatic compounds. From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich

Wavenumber (cm^{-1})	Assignment
3100–3000	C–H stretching
2000–1700	Overtone and combination bands
1600–1430	C=C stretching
1275–1000	In-plane C–H bending
900–690	Out-of-plane C–H bending

4.3 Aromatic Compounds

Aromatic compounds show useful characteristic infrared bands in five regions of the mid-infrared spectrum (Table 4.2). The C–H stretching bands of aromatic compounds appear in the 3100–3000 cm^{-1} range, so making them easy to differentiate from those produced by aliphatic C–H groups which appear below 3000 cm^{-1}. In the 2000–1700 cm^{-1} region, a series of weak combination and overtone bands appear and the pattern of the overtone bands reflects the substitution pattern of the benzene ring. Skeletal vibrations, representing C=C stretching, absorb in the 1650–1430 cm^{-1} range. The C–H bending bands appear in the regions 1275–1000 cm^{-1} (in-plane bending) and 900–690 cm^{-1} (out-of-plane bending). The bands of the out-of-plane bending vibrations of aromatic compounds are strong and characteristic of the number of hydrogens in the

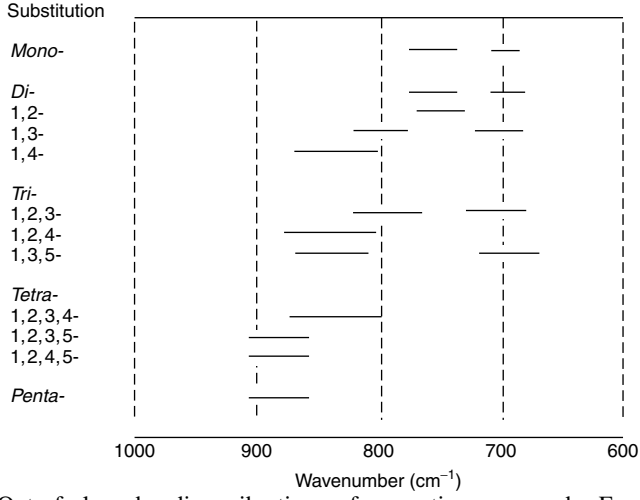

Figure 4.2 Out-of-plane bending vibrations of aromatic compounds. From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

ring, and hence can be used to give the substitution pattern. This information is summarized in Figure 4.2.

SAQ 4.3

Examine the IR spectra of three isomeric disubstituted benzenes presented below in Figures 4.3, 4.4 and 4.5. Which of these is 1,2-, which 1,3- and which 1,4-disubstituted?

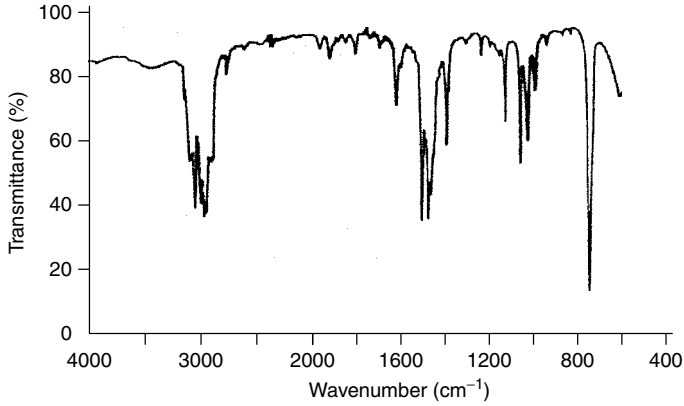

Figure 4.3 Infrared spectrum of a disubstituted benzene: compound A (cf. SAQ 4.3). From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

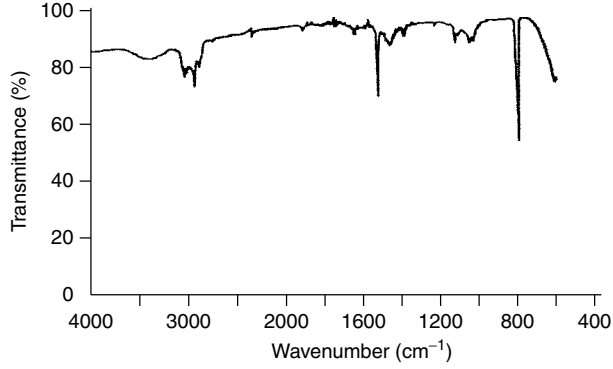

Figure 4.4 Infrared spectrum of a disubstituted benzene: compound B (cf. SAQ 4.3). From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

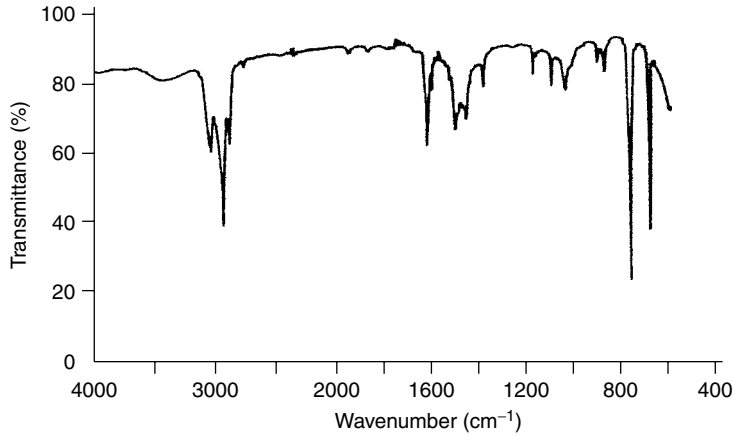

Figure 4.5 Infrared spectrum of a disubstituted benzene: compound C (cf. SAQ 4.3). From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

4.4 Oxygen-Containing Compounds

4.4.1 Alcohols and Phenols

Alcohols and phenols produce characteristic infrared bands due to O–H stretching and C–O stretching, which are both sensitive to hydrogen bonding. For alcohols, the broad O–H stretching band is centred at 3600 cm^{-1}, while for phenols this band appears 50–100 cm^{-1} lower than the alcohol wavenumber. C–O stretching in alcohols and phenols produces a strong band in the 1300–1000 cm^{-1} region. These compounds also produce O–H bending vibrations, but the latter couple with other vibrations and produce complex bands in the fingerprint region. The main bands for these compounds are shown in Table 4.3.

4.4.2 Ethers

Ethers may be identified by a strong C–O stretching band near 1100 cm^{-1} due to the C–O–C linkage in this type of compound (see Table 4.3). Aromatic ethers show a strong band near 1250 cm^{-1}, while cyclic ethers show a C–O stretching band over a broad 1250–900 cm^{-1} range.

4.4.3 Aldehydes and Ketones

Aliphatic and aromatic ketones show carbonyl bands at 1730–1700 and 1700–1680 cm^{-1}, respectively, while aliphatic and aromatic aldehydes produce carbonyl bands in the 1740–1720 cm^{-1} and 1720–1680 cm^{-1} ranges, respectively (see Table 4.3). The position of the C=O stretching wavenumber within these

Table 4.3 Characteristic infrared bands of oxygen-containing compounds

Wavenumber (cm^{-1})	Assignment
	Alcohol and phenols
3600	Alcohol O–H stretching
3550–3500	Phenol O–H stretching
1300–1000	C–O stretching
	Ethers
1100	C–O–C stretching
	Aldehydes and ketones
2900–2700	Aldehyde C–H stretching
1740–1720	Aliphatic aldehyde C=O stretching
1730–1700	Aliphatic ketone C=O stretching
1720–1680	Aromatic aldehyde C=O stretching
1700–1680	Aromatic ketone C=O stretching
	Esters
1750–1730	Aliphatic C=O stretching
1730–1705	Aromatic C=O stretching
1310–1250	Aromatic C–O stretching
1300–1100	Aliphatic C–O stretching
	Carboxylic acids
3300–2500	O–H stretching
1700	C=O stretching
1430	C–O–H in-plane bending
1240	C–O stretching
930	C–O–H out-of-plane bending
	Anhydrides
1840–1800	C=O stretching
1780–1740	C=O stretching
1300–1100	C–O stretching

ranges is dependent on hydrogen bonding and conjugation within the molecule. Conjugation with a C=C band results in delocalization of the C=O group, hence causing the absorption to shift to a lower wavenumber. Aldehydes also show a characteristic C–H stretching band in the 2900–2700 cm^{-1} range.

DQ 4.1

Examine the spectrum of 2-methylbenzaldehyde shown below in Figure 4.6 and identify the aldehyde C–H stretching band. Describe the effect responsible for the doublet formation.

Answer

Aldehydes show C–H stretching in the 2900–2700 cm^{-1} region. ***Fermi resonance*** *is responsible for the formation of the doublet. Figure 4.6 shows a doublet centred at 2780 cm^{-1} which may be assigned to aldehyde C–H stretching. This is the coupling of a* ***fundamental*** *with an* ***overtone*** *band, with the two vibrations being in the same place. As the doublet is centred at about 2780 cm^{-1}, a band near 1400 cm^{-1} is expected to be the fundamental. There is a doublet in this region with peaks at 1382 and 1386 cm^{-1}. One of these is a CH_3 bending band, while the other is an H–C–O in-plane bending band. The latter must be responsible for the doublet since the CH_3 bending band is not in the same plane as the aldehyde C–H stretching movement. Twice 1386 cm^{-1} is 2772 cm^{-1}, which is close to the centre of the observed doublet.*

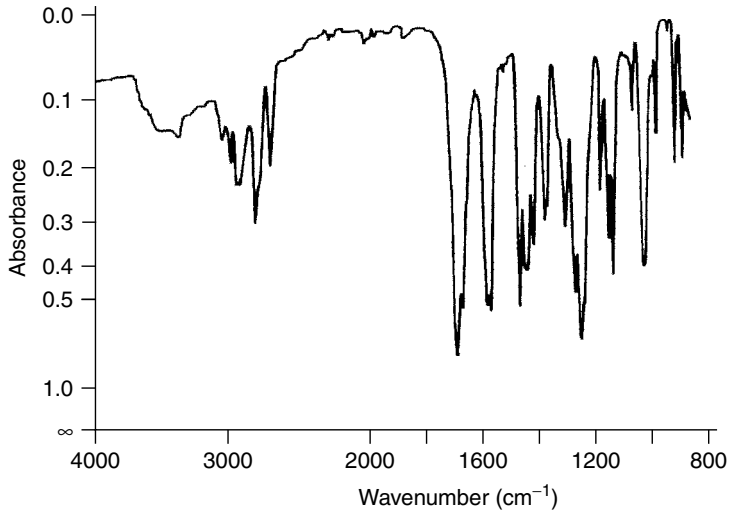

Figure 4.6 Infrared spectrum of 2-methoxybenzaldehyde (cf. DQ 4.1).

4.4.4 Esters

The two most polar bonds in esters (containing the –CO–O–C–unit) are the C=O and C–O bonds and these bonds produce the strongest bands in the spectrum of any ester (summarized in Table 4.3). Aromatic and aliphatic esters may be differentiated, as both C=O stretching and C–O stretching vibrations produce bands in different ranges: aliphatic esters produce C=O and C–O bands at 1750–1730 and 1300–1100 cm^{-1}, respectively, while aromatic esters produce C=O and C–O bands at 1730–1705 and 1310–1250 cm^{-1}, respectively.

4.4.5 Carboxylic Acids and Anhydrides

Carboxylic acids (RCOOH) exist as dimers, except in dilute solution, due to strong intermolecular hydrogen bonding. Carboxylic acids show a strong broad O–H stretching band in the 3300–2500 cm^{-1} range. The C=O stretching band of the dimer is observed near 1700 cm^{-1}, while the free acid band is observed at higher wavenumbers (1760 cm^{-1}). In addition, carboxylic acids show characteristic C–O stretching and in-plane and out-of-plane O–H bending bands at 1240, 1430 and 930 cm^{-1}, respectively.

Anhydrides (–CO–O–CO–) may be identified by a distinctive carbonyl band region. A strong doublet is observed in this region with components in the 1840–1800 and 1780–1740 cm^{-1} ranges. Anhydrides also show a strong C–O stretching band near 1150 cm^{-1} for open-chain anhydrides and at higher wavenumbers for cyclic structures. Table 4.3 summarizes the major infrared bands observed for carboxylic acids and anhydrides.

SAQ 4.4

Assign the following pairs of carbonyl stretching wavenumbers to the corresponding structures shown below in Figure 4.7: 1815 and 1750 cm^{-1}, and 1865 and 1780 cm^{-1}.

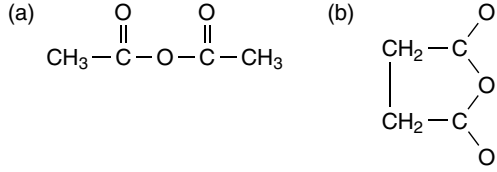

Figure 4.7 Anhydride structures (cf. SAQ 4.4).

DQ 4.2

Given that a molecule contains oxygen, how could an infrared spectrum of such a molecule be used to find out whether the compound was a carboxylic acid, a phenol, an alcohol or an ether?

Answer

Ethers can easily be identified because they are the only compounds of the four that do not absorb above 3200 cm^{-1}. Carboxylic acids have a very broad absorption from the O–H stretching between 2500 and 3500 cm^{-1}. They are readily distinguished from alcohols and phenols where the O–H absorption bands are not as broad as those of carboxylic acids. Both

phenols and alcohols absorb in the O–H stretching region and can only be differentiated by the benzene ring absorption of the phenol. If the alcohol is an aromatic alcohol, a new approach is required and an additional chemical test will be required.

4.5 Nitrogen-Containing Compounds

4.5.1 Amines

Primary (–NH_2), secondary (–NH) and tertiary (no hydrogen attached to N) amines may be differentiated by using infrared spectra. Primary amines have two sharp N–H stretching bands near 3335 cm^{-1}, a broad NH_2 scissoring band at 1615 cm^{-1}, and NH_2 wagging and twisting bands in the 850–750 cm^{-1} range. Secondary amines show only one N–H stretching band at 3335 cm^{-1} and an N–H bending band at 1615 cm^{-1}. The N–H wagging band for secondary amines appears at 715 cm^{-1}. Tertiary amines are characterized by an N–CH_2 stretching band at 2780 cm^{-1}. All amines show C–N stretching bands, with aromatic amines showing such bands in the 1360–1250 cm^{-1} range and aliphatic amines showing bands at 1220–1020 cm^{-1}. Table 4.4 summarizes the main infrared bands for amines.

Table 4.4 Characteristic infrared bands of amines

Wavenumber (cm^{-1})	Assignment
3335	N–H stretching (doublet for primary amines; singlet for secondary amines)
2780	N–CH_2 stretching
1615	NH_2 scissoring, N–H bending
1360–1250	Aromatic C–N stretching
1220–1020	Aliphatic C–N stretching
850–750	NH_2 wagging and twisting
715	N–H wagging

SAQ 4.5

Figure 4.8 below shows the infrared spectrum of a liquid film of hexylamine. Assign the major bands appearing in this spectrum.

4.5.2 Amides

Primary amides (–CO–NH–) display two strong NH_2 stretching bands, i.e. asymmetric stretching at 3360–3340 cm^{-1} and symmetric stretching at

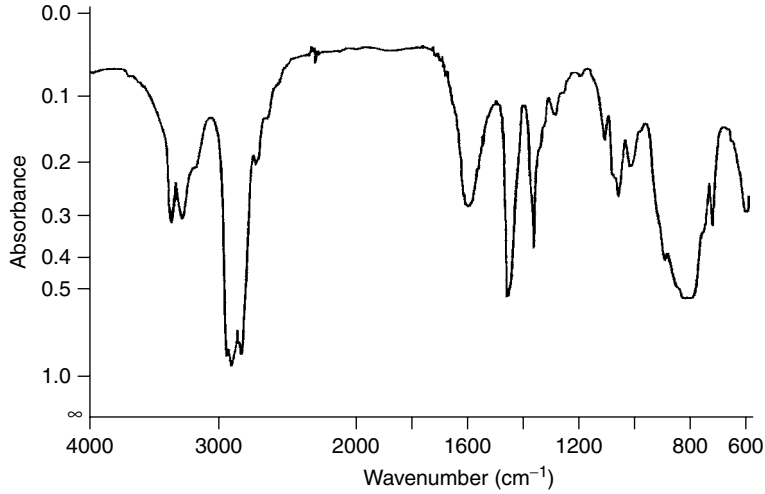

Figure 4.8 Infrared spectrum of hexylamine (cf. SAQ 4.5). From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

3190–3170 cm^{-1}. They also exhibit C=O stretching at 1680–1660 cm^{-1} (referred to as the amide I band) and NH_2 bending at 1650–1620 cm^{-1} (referred to as the amide II band). Secondary amides show an N–H stretching band at 3300–3250 cm^{-1}, while the carbonyl stretching (amide I band) is observed at 1680–1640 cm^{-1}. The amide II band for secondary amides is due to the coupling of N–H bending and C–N stretching and appears at 1560–1530 cm^{-1}. A weak band which is an overtone of the amide II band appears at 3100–3060 cm^{-1}. A broad N–H wagging band also appears at 750–650 cm^{-1}. Table 4.5 summarizes the infrared bands of primary and secondary amides.

Table 4.5 Characteristic infrared bands of amides

Wavenumber (cm^{-1})	Assignment
3360–3340	Primary amide NH_2 asymmetric stretching
3300–3250	Secondary amide N–H stretching
3190–3170	Primary amide NH_2 symmetric stretching
3100–3060	Secondary amide amide II overtone
1680–1660	Primary amide C=O stretching
1680–1640	Secondary amide C=O stretching
1650–1620	Primary amide NH_2 bending
1560–1530	Secondary amide N–H bending, C–N stretching
750–650	Secondary amide N–H wagging

Table 4.6 Characteristic infrared bands of various nitrogen-containing compounds

Wavenumber (cm^{-1})	Assignment
2260–2240	Aliphatic nitrile C≡N stretching
2240–2220	Aromatic nitrile C≡N stretching
2180–2110	Aliphatic isonitrile –N≡C stretching
2160–2120	Azide N≡N stretching
2130–2100	Aromatic isonitrile –N≡C stretching
1690–1620	Oxime C=N–OH stretching
1680–1650	Nitrite N=O stretching
1660–1620	Nitrate NO_2 asymmetric stretching
1615–1565	Pyridine C=N stretching, C=C stretching
1560–1530	Aliphatic nitro compound NO_2 asymmetric stretching
1540–1500	Aromatic nitro compound NO_2 asymmetric stretching
1450–1400	Azo compound N=N stretching
1390–1370	Aliphatic nitro compound NO_2 symmetric stretching
1370–1330	Aromatic nitro compound NO_2 symmetric stretching
1300–1270	Nitrate NO_2 symmetric stretching
965–930	Oxime N–O stretching
870–840	Nitrate N–O stretching
710–690	Nitrate NO_2 bending

Other nitrogen-containing compounds, such as nitriles, azides, oximes, nitrites and pyridines, also show characteristic infrared bands which may be used for identification purposes. These bands are summarized in Table 4.6.

4.6 Halogen-Containing Compounds

Table 4.7 lists the absorption regions observed for organic halogen compounds. Particular care must be taken when fluorine is present in a compound as the C–F stretching bands, observed between 1350 and 1100 cm^{-1}, are very strong and may obscure any C–H bands that might be present.

Table 4.7 Characteristic infrared bands of organic halogen compounds

Wavenumber (cm^{-1})	Assignment
1300–1000	C–F stretching
800–400	C–X stretching (X = F, Cl, Br or I)

4.7 Heterocyclic Compounds

Heterocyclic compounds, such as pyridines, pyrazines, pyrroles and furanes, show C–H stretching bands in the 3080–3000 cm^{-1} region. For heterocyclic compounds containing an N–H group, an N–H stretching band is observed in the 3500–3200 cm^{-1} region, the position of which depends upon the degree of hydrogen bonding. These compounds show characteristic band patterns in the 1600–1300 cm^{-1} ring stretching region. The nature of the substituents affects the pattern. In addition, the pattern of out-of-plane C–H bending bands in the 800–600 cm^{-1} region are characteristic for heterocyclic molecules.

4.8 Boron Compounds

Compounds containing the B–O linkage, such as boronates and boronic acids, are characterized by a strong B–O stretching mode at 1380–1310 cm^{-1}. Boronic acid and boric acid contain OH groups and so show a broad O–H stretching mode in the 3300–3200 cm^{-1} region. Compounds with a B–N group, such as borazines and amino boranes, show a strong absorption in the 1465–1330 cm^{-1} region due to B–N stretching. B–H stretching, due to BH and BH_2 groups, produces bands in the 2650–2350 cm^{-1} range. The BH_2 absorption is usually a doublet due to symmetric and asymmetric vibrations. There is also a B–H bending band in the 1205–1140 cm^{-1} region and a wagging band at 980–920 cm^{-1} due to the BH_2 group. Table 4.8 provides a summary of the main infrared modes in boron compounds.

4.9 Silicon Compounds

Silicon compounds show characteristic Si–H bands. The Si–H stretching bands appear at 2250–2100 cm^{-1}. The Si–CH_3 band gives rise to a symmetric CH_3

Table 4.8 Characteristic infrared bands of boron compounds. From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich

Wavenumber (cm^{-1})	Assignment
3300–3200	B–O–H stretching
2650–2350	B–H stretching
1465–1330	B–N stretching
1380–1310	B–O stretching
1205–1140	B–H bending
980–920	B–H wagging

Table 4.9 Characteristic infrared bands of silicon compounds

Wavenumber (cm^{-1})	Assignment
3700–3200	Si–OH stretching
2250–2100	Si–H stretching
1280–1250	Si–CH_3 symmetric bending
1430, 1110	Si–C_6H_5 stretching
1130–1000	Si–O–Si asymmetric stretching
1110–1050	Si–O–C stretching

bending band in the 1280–1250 cm^{-1} range. The O–H stretching bands of Si–OH groups appear in the same region as alcohols, i.e. 3700–3200 cm^{-1}. Si–O–C stretching produces a broad band at 1100–1050 cm^{-1} and siloxanes also show a strong band at 1130–1000 cm^{-1}. Silicon attached to a benzene ring produces two strong bands near 1430 and 1110 cm^{-1}. Some of the common infrared modes of silicon compounds are summarized in Table 4.9.

4.10 Phosphorus Compounds

Phosphorus acids and esters possess P–OH groups which produce one or two broad bands in the 2700–2100 cm^{-1} region. Aliphatic phosphorus compounds

Table 4.10 Characteristic infrared bands of phosphorus compounds

Wavenumber (cm^{-1})	Assignment
2425–2325	Phosphorus acid and ester P–H stretching
2320–2270	Phosphine P–H stretching
1090–1080	Phosphine PH_2 bending
990–910	Phosphine P–H wagging
2700–2100	Phosphorus acid and ester O–H stretching
1040–930	Phosphorus ester P–OH stretching
1050–950	Aliphatic asymmetric P–O–C stretching
830–750	Aliphatic symmetric P–O–C stretching
1250–1160	Aromatic P–O stretching
1050–870	Aromatic P–O stretching
1450–1430	Aromatic P–C stretching
1260–1240	Aliphatic P=O stretching
1350–1300	Aromatic P=O stretching
1050–700	P–F stretching
850–500	P=S stretching
600–300	P–Cl stretching
500–200	P–Br stretching
500–200	P–S stretching

containing a P–O–C link show a strong band between 1050 and 950 cm^{-1} due to asymmetric stretching. If a P=O group is present in an aliphatic phosphorus compound, a strong band near 1250 cm^{-1} is observed. Aromatic phosphorus compounds show characteristic bands that enable them to be differentiated from aliphatic compounds. A strong sharp band near 1440 cm^{-1} appears for compounds where the phosphorus atom is directly attached to the benzene ring. Where the P–O group is attached to the ring, two bands appear in the 1250–1160 cm^{-1} and 1050–870 cm^{-1} regions due to P–O stretching. When the P–O group is attached to the ring via the oxygen, two bands also appear, but the higher-wavenumber band is observed between 1350 and 1250 cm^{-1}. Table 4.10 summarizes the important infrared bands of some common phosphorus compounds.

SAQ 4.6

Figure 4.9 below shows the spectrum of a phosphorus compound with the empirical formula $C_2H_7PO_3$. Assign the major infrared bands in this spectrum.

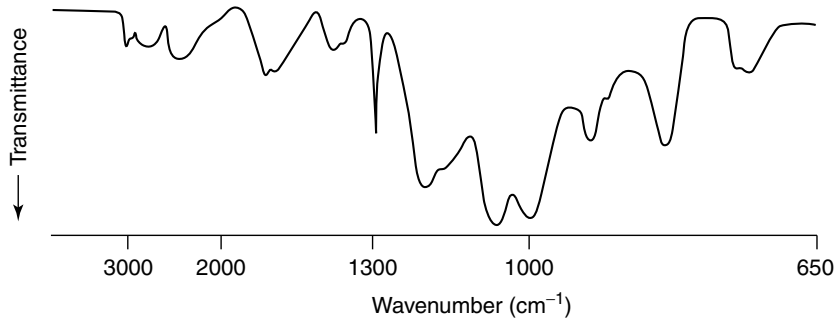

Figure 4.9 Infrared spectrum of an unknown phosphorus compound ($C_2H_7PO_3$) (cf. SAQ 4.6). Reproduced by permission of J. Emsley and D. Hall, from *The Chemistry of Phosphorus*, Harper and Row, London, p. 107 (1976).

4.11 Sulfur Compounds

The SO_2 and SO groups of sulfur compounds produce strong infrared bands in the 1400–1000 cm^{-1} range. The expected S=O stretching bands for sulfoxides, sulfones, sulfonic acids, sulfonamides, sulfonyl chlorides and sulfonates are given in Table 4.11. The other bonds involving sulfur, such as S–H, S–S and C–S, produce weaker infrared bands. Compounds, such as sulfides and mercaptans,

Table 4.11 Characteristic infrared bands of sulfur compounds

Wavenumber (cm^{-1})	Assignment
700–600	C–S stretching
550–450	S–S stretching
2500	S–H stretching
1390–1290	SO_2 asymmetric stretching
1190–1120	SO_2 symmetric stretching
1060–1020	S=O stretching

containing C–S and S–S bonds, show stretching bands at 700–600 cm^{-1} and near 500 cm^{-1}, respectively. The weak S–H stretching band appears near 2500 cm^{-1}.

4.12 Near-Infrared Spectra

As near-infrared spectra are, for the most part, the result of overtone bands of fundamental groups containing C–H, O–H and N–H bonds, organic molecules may be investigated by using this approach [6, 7]. Near-infrared (NIR) spectroscopy can be an attractive option for certain organic systems because of ease of sampling. Table 4.12 summarizes the bands commonly observed for organic molecules in the near-infrared region.

For aliphatic hydrocarbons, the first overtones of C–H stretching are observed in the 1600–1800 nm range, the second overtones at 1150–1210 nm and the third overtones at 880–915 nm. NIR spectroscopy may be used to study unsaturated hydrocarbons. Although bands due to C=C and C≡C bonds are not directly observed in the near infrared, the bands due to the adjacent C–H bonds may be differentiated from saturated hydrocarbons.

Table 4.12 Common near-infrared bands of organic compounds

Wavelength (nm)	Assignment
2200–2450	Combination C–H stretching
2000–2200	Combination N–H stretching, combination O–H stretching
1650–1800	First overtone C–H stretching
1400–1500	First overtone N–H stretching, first overtone O–H stretching
1300–1420	Combination C–H stretching
1100–1225	Second overtone C–H stretching
950–1100	Second overtone N–H stretching, second overtone O–H stretching
850–950	Third overtone C–H stretching
775–850	Third overtone N–H stretching

Aromatic hydrocarbons produce different bands in the near infrared to those of aliphatic hydrocarbons. The first and second overtone C–H stretching bands for aromatic compounds are seen in the 1600–1800 nm and 1100–1250 nm regions, respectively. They also show a series of combination bands at 2100–2250 nm and 2450–2500 nm. Ring-substitution patterns affect the positions of these bands.

SAQ 4.7

Figure 4.10 below shows the NIR spectrum of benzene. Identify the major bands that appear in this spectrum.

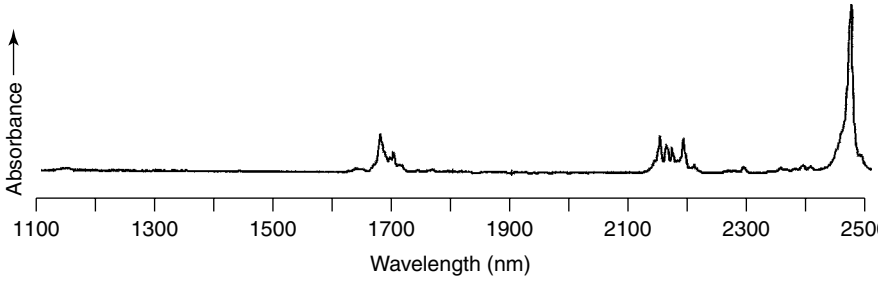

Figure 4.10 NIR spectrum of benzene (cf. SAQ 4.7). From Weyer, L. G. and Lo, S. C., 'Spectra–Structure Correlations in the Near-Infrared', in *Handbook of Vibrational Spectroscopy*, Vol. 3, Chalmers, J. M. and Griffiths, P. R. (Eds), pp. 1817–1837. Copyright 2002. © John Wiley & Sons Limited. Reproduced with permission.

For organic compounds containing C–O bonds, these groups affect the spectra by causing shifts in the bands of adjacent C–H, O–H and N–H groups. Alcohols and organic acids show combination and overtone O–H stretching bands in the 1900–2200 nm and 1400–1650 nm regions. The positions and shapes of these bands are significantly influenced by the degree of hydrogen bonding in such molecules.

Primary amines show characteristic first overtone bands at 1450, 1550 and 1000 nm which represent the first and second overtones of N–H stretching bands. Tertiary amines produce no N–H overtones, but do produce C–H and O–H stretching combination bands at 1260–1270 nm. The first overtones of the N–H stretching bands of aliphatic amines are shifted to lower wavelengths. Primary amides may be characterized by combination bands at 1930–2250 nm and an N–H stretching overtone band at 1450–1550 nm. Secondary amides produce overtone bands in the 1350–1550 nm region and combination bands in the 1990–2250 nm region.

4.13 Identification

This section provides a number of examples to illustrate approaches to the identification of unknown organic materials by using infrared spectroscopy. First, an example of the use of the technique in identifying an organic compound containing a number of functional groups is provided.

Citronellal is the terpenoid responsible for the characteristic aroma of lemon oil, and is used in perfumes and as a mosquito repellent. The infrared spectrum of citronellal is shown in Figure 4.11. At the higher-wavenumber end of the spectrum, the C–H stretching region provides important information about the citronellal structure. This region is intense, hence indicating the presence of a number of C–H groups in the structure. Distinct C–H stretching modes at 2800 and 2700 cm^{-1} appear at wavenumbers characteristic of aldehydes. In addition, a strong band at 1730 cm^{-1} confirms the presence of an aldehyde group. The other C–H stretching modes appear in the 3000–2900 cm^{-1} range and can be attributed to aliphatic C–H stretching. The lack of bands at wavenumbers greater than 3000 cm^{-1} suggests that there is no aromatic group in the citronellal structure. The structure of citronellal is illustrated in Figure 4.12.

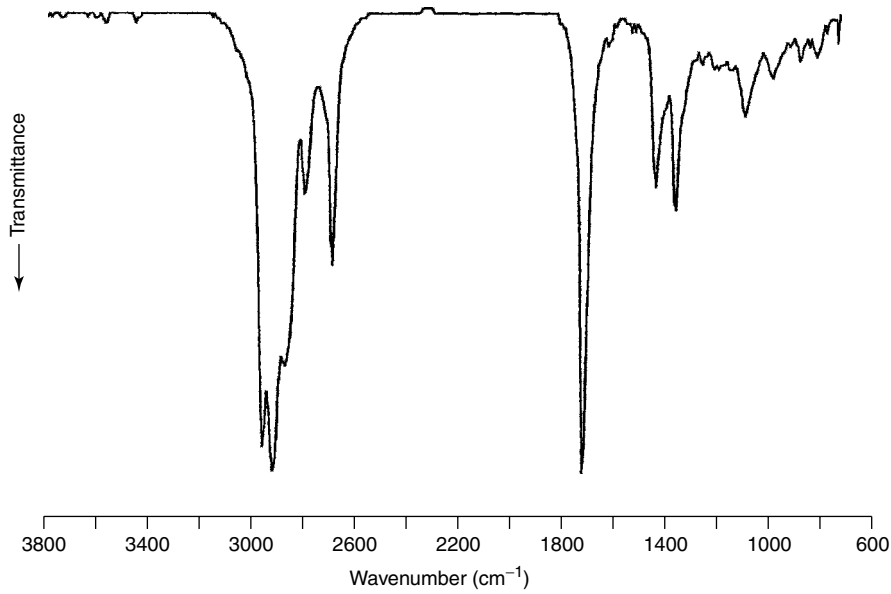

Figure 4.11 Infrared spectrum of citronellal. From Stuart, B., *Biological Applications of Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1997. © University of Greenwich, and reproduced by permission of the University of Greenwich.

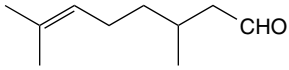

Figure 4.12 Structure of citronellal.

A series of SAQs is now provided for practice in the assignment of infrared bands and for the determination of structures by using infrared spectra.

SAQ 4.8

The infrared spectrum of vanillin is shown below in Figure 4.13. Vanillin occurs naturally in vanilla and is used as a flavouring agent. Identify the functional groups in this molecule.

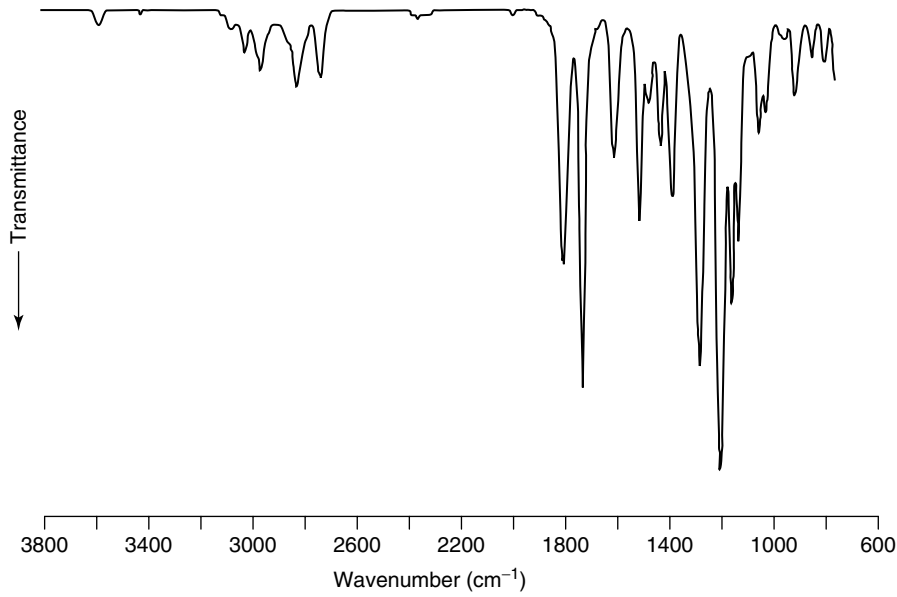

Figure 4.13 Infrared spectrum of vanillin (cf. SAQ 4.8). From Stuart, B., *Biological Applications of Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1997. © University of Greenwich, and reproduced by permission of the University of Greenwich.

SAQ 4.9

Figure 4.14 below illustrates the infrared spectrum of a liquid film of a compound with the structural formula C_7H_9N. Assign the major infrared bands of this compound, and suggest a possible structure consistent with this spectrum.

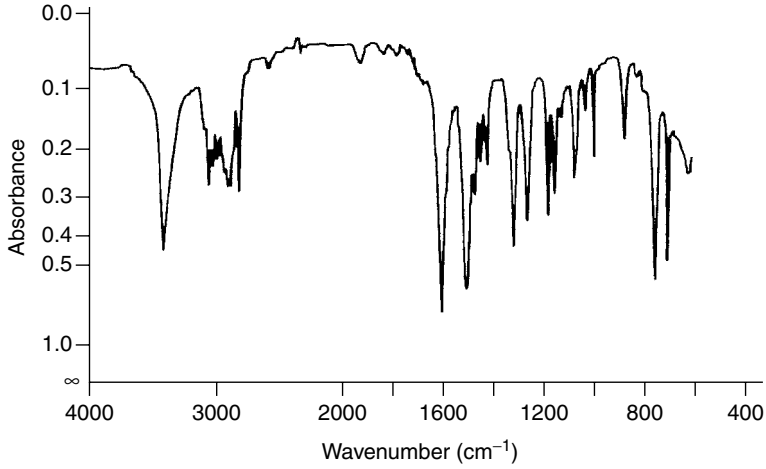

Figure 4.14 Infrared spectrum of an unknown compound (C_7H_9N) (cf. SAQ 4.9).

SAQ 4.10

The infrared spectrum of a liquid organic compound ($C_{10}H_{22}$) is shown below in Figure 4.15. Identify this compound.

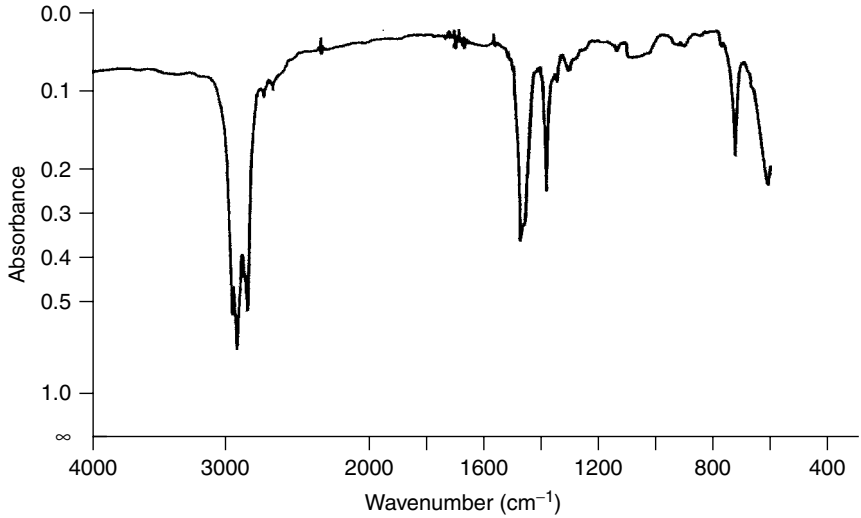

Figure 4.15 Infrared spectrum of an unknown hydrocarbon ($C_{10}H_{22}$) (cf. SAQ 4.10). From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

SAQ 4.11

The infrared spectrum of an organic compound ($C_4H_{10}O$) is shown below in Figure 4.16. Identify this compound.

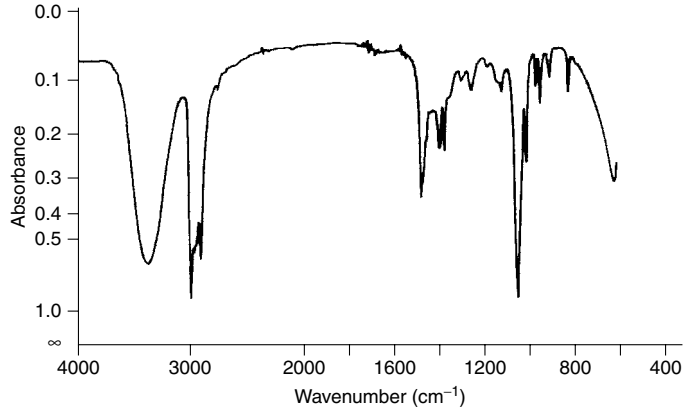

Figure 4.16 Infrared spectrum of an unknown liquid ($C_4H_{10}O$) (cf. SAQ 4.11). From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

SAQ 4.12

The infrared spectrum of an organic compound (C_8H_{16}) is shown below in Figure 4.17. Identify this compound.

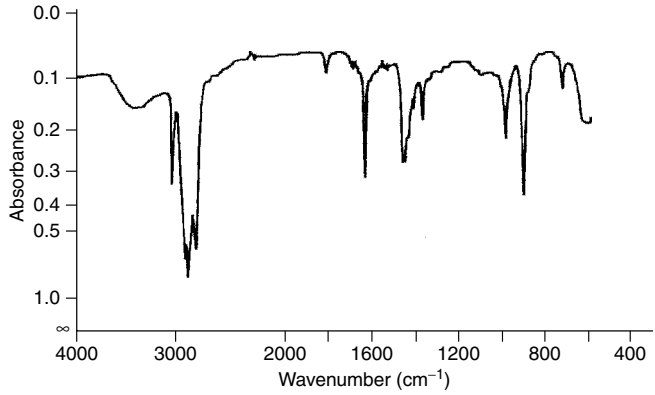

Figure 4.17 Infrared spectrum of an unknown hydrocarbon (C_8H_{16}) (cf. SAQ 4.12). From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

SAQ 4.13

The infrared spectrum of an organic compound is shown below in Figure 4.18. Identify this compound.

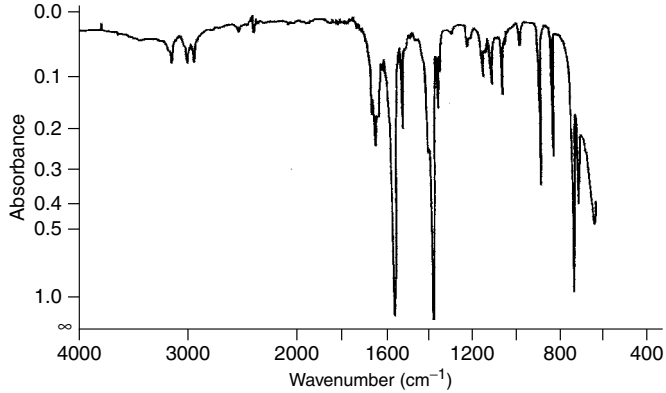

Figure 4.18 Infrared spectrum of an unknown organic liquid (cf. SAQ 4.13). From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

SAQ 4.14

The infrared spectrum of an organic compound (C_7H_7NO) in chloroform solution is shown below in Figure 4.19. Identify this compound.

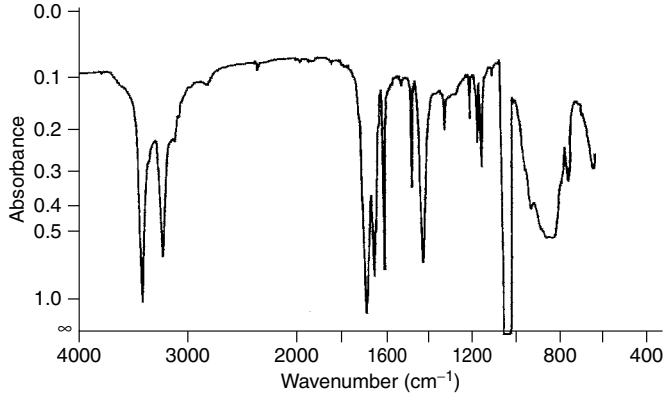

Figure 4.19 Infrared spectrum of an unknown compound (C_7H_7NO) in chloroform solution (cf. SAQ 4.14). From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich.

Summary

This chapter has provided a review of the major infrared bands associated with common classes of organic molecules. Examples were provided in order to use this information to assign the infrared bands of a range of organic molecules and to determine the structures of such molecules. This information may then be further utilized to characterize the infrared spectra obtained for various other organic compounds, for example, polymeric and biological materials and those used in industrial applications. The latter are introduced in Chapters 6, 7 and 8, respectively.

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