INFRARED SPECTROSCOPY: FUNDAMENTALS AND APPLICATIONS

Barbara H. Stuart
University of Technology, Sydney, Australia

John Wiley & Sons, Ltd

INFRARED SPECTROSCOPY: FUNDAMENTALS AND APPLICATIONS

Analytical Techniques in the Sciences (AnTS)

Series Editor: David J. Ando, Consultant, Dartford, Kent, UK

A series of open learning/distance learning books which covers all of the major analytical techniques and their application in the most important areas of physical, life and materials sciences.

Titles Available in the Series

Analytical Instrumentation: Performance Characteristics and Quality
Graham Currell, University of the West of England, Bristol, UK

Fundamentals of Electroanalytical Chemistry
Paul M. S. Monk, Manchester Metropolitan University, Manchester, UK

Introduction to Environmental Analysis
Roger N. Reeve, University of Sunderland, Sunderland, UK

Polymer Analysis
Barbara H. Stuart, University of Technology, Sydney, Australia

Chemical Sensors and Biosensors
Brian R. Eggins, University of Ulster at Jordanstown, Northern Ireland, UK

Methods for Environmental Trace Analysis
John R. Dean, Northumbria University, Newcastle, UK

Liquid Chromatography–Mass Spectrometry: An Introduction
Robert E. Ardrey, University of Huddersfield, Huddersfield, UK

The Analysis of Controlled Substances
Michael D. Cole, Anglia Polytechnic University, Cambridge, UK

Infrared Spectroscopy: Fundamentals and Applications
Barbara H. Stuart, University of Technology, Sydney, Australia

Forthcoming Titles

Practical Inductively Coupled Plasma Spectroscopy
John R. Dean, Northumbria University, Newcastle, UK

Techniques of Modern Organic Mass Spectrometry
Robert E. Ardrey, University of Huddersfield, Huddersfield, UK

INFRARED SPECTROSCOPY: FUNDAMENTALS AND APPLICATIONS

Barbara H. Stuart
University of Technology, Sydney, Australia

John Wiley & Sons, Ltd

Telephone (+44) 1243 779777

Email (for orders and customer service enquiries): cs-books@wiley.co.uk
Visit our Home Page on www.wileyeurope.com or www.wiley.com

Other Wiley Editorial Offices

John Wiley & Sons Inc., 111 River Street, Hoboken, NJ 07030, USA

Jossey-Bass, 989 Market Street, San Francisco, CA 94103-1741, USA

Wiley-VCH Verlag GmbH, Boschstr. 12, D-69469 Weinheim, Germany

John Wiley & Sons Australia Ltd, 33 Park Road, Milton, Queensland 4064, Australia

John Wiley & Sons (Asia) Pte Ltd, 2 Clementi Loop #02-01, Jin Xing Distripark, Singapore 129809

John Wiley & Sons Canada Ltd, 22 Worcester Road, Etobicoke, Ontario, Canada M9W 1L1

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic books.

Library of Congress Cataloging-in-Publication Data

Stuart, Barbara (Barbara H.)
Infrared spectroscopy : fundamentals and applications / Barbara H. Stuart.
p. cm.–(Analytical techniques in the sciences)
Includes bibliographical references and index.
ISBN 0-470-85427-8 (acid-free paper)–ISBN 0-470-85428-6 (pbk. : acid-free paper)
1. Infrared spectroscopy. I. Title. II. Series.
QD96.15S76 2004
543′.57–dc22
2003027960

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

ISBN 0-470-85427-8 (Cloth)
ISBN 0-470-85428-6 (Paper)

Typeset in 10/12pt Times by Laserwords Private Limited, Chennai, India
Printed and bound in Great Britain by Antony Rowe Ltd, Chippenham, Wiltshire
This book is printed on acid-free paper responsibly manufactured from sustainable forestry in which at least two trees are planted for each one used for paper production.

Contents

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,

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

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

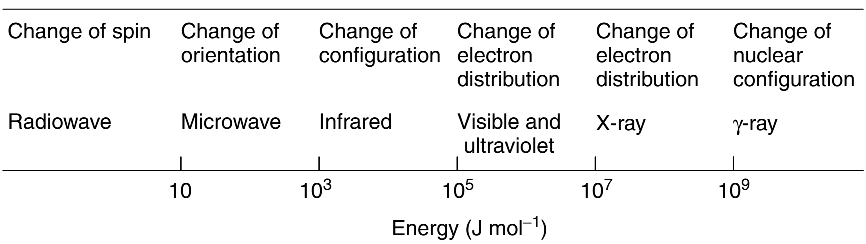

Figure 1.1 Regions of the electromagnetic spectrum. From Stuart, B., *Biological Applications of Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1997. © University of Greenwich, and reproduced by permission of the University of Greenwich.

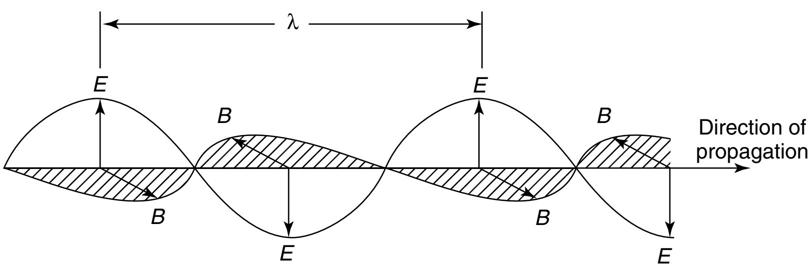

Figure 1.2 Representation of an electromagnetic wave. Reproduced from Brittain, E. F. H., George, W. O. and Wells, C. H. J., *Introduction to Molecular Spectroscopy*, Academic Press, London, Copyright (1975), with permission from Elsevier.

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

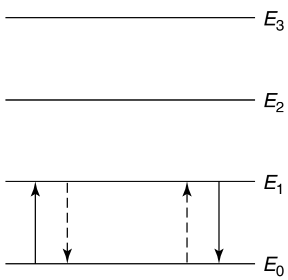

Figure 1.3 Illustration of quantized discrete energy levels.

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.