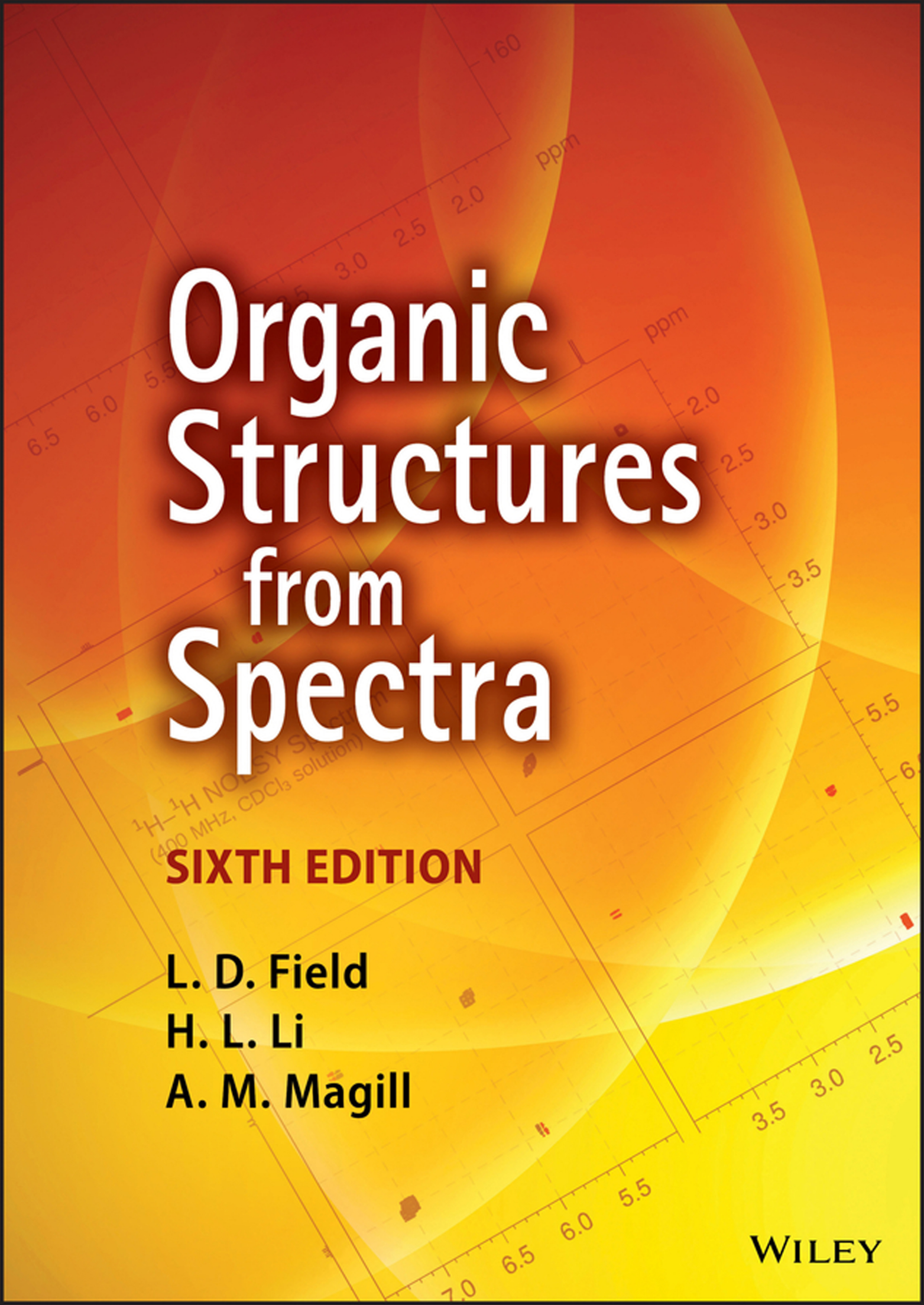


Organic Structures from Spectra

SIXTH EDITION

L. D. Field
H. L. Li
A. M. Magill

WILEY

Organic Structures from Spectra

Sixth Edition

Organic Structures from Spectra

Sixth Edition

L. D. Field
Professor of Chemistry
School of Chemistry
University of New South Wales, Australia

H. L. Li
Senior Research Associate
School of Chemistry
University of New South Wales, Australia

A. M. Magill
Honorary Research Associate
School of Chemistry
University of New South Wales, Australia

WILEY

This edition first published 2020
© 2020 John Wiley & Sons Ltd

Edition History
John Wiley & Sons (4e, 2008)
John Wiley & Sons (5e, 2013)

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, except as permitted by law. Advice on how to obtain permission to reuse material from this title is available at http://www.wiley.com/go/permissions.

The right of L. D. Field, H. L. Li and A. M. Magill to be identified as the authors of this work has been asserted in accordance with law.

Registered Offices
John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, USA
John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, UK

Editorial Office
John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, UK

For details of our global editorial offices, customer services, and more information about Wiley products visit us at www.wiley.com.

Wiley also publishes its books in a variety of electronic formats and by print-on-demand. Some content that appears in standard print versions of this book may not be available in other formats.

Limit of Liability/Disclaimer of Warranty
In view of ongoing research, equipment modifications, changes in governmental regulations, and the constant flow of information relating to the use of experimental reagents, equipment, and devices, the reader is urged to review and evaluate the information provided in the package insert or instructions for each chemical, piece of equipment, reagent, or device for, among other things, any changes in the instructions or indication of usage and for added warnings and precautions. While the publisher and authors have used their best efforts in preparing this work, they make no representations or warranties with respect to the accuracy or completeness of the contents of this work and specifically disclaim all warranties, including without limitation any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives, written sales materials or promotional statements for this work. The fact that an organization, website, or product is referred to in this work as a citation and/or potential source of further information does not mean that the publisher and authors endorse the information or services the organization, website, or product may provide or recommendations it may make. This work is sold with the understanding that the publisher is not engaged in rendering professional services. The advice and strategies contained herein may not be suitable for your situation. You should consult with a specialist where appropriate. Further, readers should be aware that websites listed in this work may have changed or disappeared between when this work was written and when it is read. Neither the publisher nor authors shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

Library of Congress Cataloging-in-Publication Data
Names: Field, L. D., author.
Title: Organic structures from spectra / L.D. Field, Professor of Chemistry, School of Chemistry, University of New South Wales, H.L. Li, Senior Research Fellow, School of Chemistry, University of New South Wales, A.M. Magill, Honorary Research Fellow, School of Chemistry, University of New South Wales.
Description: Sixth edition. | Hoboken, NJ : Wiley, 2020. | Includes bibliographical references and index.
Identifiers: LCCN 2020004972 (print) | LCCN 2020004973 (ebook) | ISBN 9781119524809 (paperback) | ISBN 9781119524793 (adobe pdf) | ISBN 9781119524847 (epub)
Subjects: LCSH: Spectrum analysis–Problems, exercises, etc. | Organic compounds–Structure–Problems, exercises, etc.
Classification: LCC QD272.S6 S74 2020 (print) | LCC QD272.S6 (ebook) | DDC 543/.17—dc23
LC record available at https://lccn.loc.gov/2020004972
LC ebook record available at https://lccn.loc.gov/2020004973

Cover Design: Wiley
Cover Image: Courtesy of Professor L. D. Field, Dr. Hsiu Lin Li and Dr. Alison Magill; © Chernookaya/Shutterstock

Set in 12/16pt TimesNewRomanMTStd by SPi Global, Chennai, India

10 9 8 7 6 5 4 3 2 1

CONTENTS

PREFACE

This is the Sixth Edition of the text "Organic Structures from Spectra". The original text, published in 1986 by J R Kalman and S Sternhell, was a remarkable instructive text at a time where spectroscopic analysis, particularly NMR spectroscopy, was becoming widespread and routinely available in many chemical laboratories. The original text was founded on the premise that the best way to learn to obtain "structures from spectra" is to build up skills by practising on simple problems. Editions two through five of the text have been published at about five-yearly intervals and each revision has taken account of new developments in spectroscopy as well as dropping out techniques that have become less important or obsolete over time. The collection has grown substantially and we are deeply indebted to Dr John Kalman and to Emeritus Professor Sev Sternhell for their commitment and contribution to all of the previous editions of "Organic Structures from Spectra".

Edition Six of the text has been expanded to include a new selection of problems and many of the problems now incorporate 2D NMR spectra (COSY, TOCSY, NOESY, C–H Correlation spectroscopy or HMBC).

The overarching philosophy remains the same as in previous editions of the text:

(a) Theoretical exposition is kept to a minimum, consistent with gaining an understanding of those aspects of the various spectroscopic techniques which are actually used in solving problems. Experience tells us that both mathematical detail and in-depth theoretical description of advanced techniques merely confuse or overwhelm the average student.

(b) The learning of data is kept to a minimum. There are now many sources of spectroscopic data available online. It is much more important to learn to use a range of generalised data well, rather than to achieve a superficial acquaintance with extensive sets of data. This book contains summary tables of essential spectroscopic data and these tables become critical reference material, particularly in the early stages of gaining experience in solving problems.

(c) We emphasise the concept of identifying "structural elements or fragments" and building the logical thought processes needed to produce a structure out of the structural elements.

The derivation of structural information from spectroscopic data is now an integral part of Organic Chemistry courses at all universities. At the undergraduate level, the principal aim is to teach students to solve simple structural problems efficiently by using combinations of the major spectroscopic techniques (UV, IR, NMR and MS). We have evolved courses both at the University of New South Wales and at the University of Sydney which achieve this aim quickly and painlessly. The text is tailored specifically to the needs and approach of these courses.

The courses have been taught in the second and third years of undergraduate chemistry, at which stage students have usually completed an elementary course of Organic Chemistry in their first year and students have also been exposed to elementary spectroscopic theory, but are, in general, unable to relate the theory to actually solving spectroscopic problems.

We have delivered courses of about 9 lectures outlining the basic theory, instrumentation and the structure–spectra correlations of the major spectroscopic techniques. The treatment is highly condensed and elementary and, not surprisingly, the students do initially have great difficulties in solving even the simplest problems. The lectures are followed by a series of problem solving workshops (about 2 hours each) with a focus on 5 to 6 problems per session. The students are permitted to work either individually or in groups and may use any additional resource material that they can find. At the conclusion of the course, the great majority of the class is quite proficient and has achieved a satisfactory level of understanding of all methods used. Clearly, most of the real teaching is done during the hands-on problem seminars. At the end of the course, there is an examination usually consisting essentially of 3 or 4 problems from the book and the results are generally very satisfactory. The students have always found this a rewarding course since the practical skills acquired are obvious to them. Solving these real puzzles is also addictive – there is a real sense of achievement, understanding and satisfaction, since the challenge in solving the graded problems builds confidence even though the more difficult examples are quite demanding.

Problems 1–19 are introductory questions designed to develop the understanding of molecular symmetry, the analysis of simple spin systems as well as how to navigate the common 2D NMR experiments.

Problems 20–294 are of the standard "structures from spectra" type and are arranged roughly in order of increasing difficulty. A number of problems deal with related compounds (sets of isomers) which differ mainly in symmetry or the connectivity of the structural elements and are ideally set together. The sets of related examples include Problems 33 and 34; 35 and 36; 40–43; 52 and 53; 57–61; 66–71; 72 and 73; 74–77; 82 and 83; 84–86; 92–94; 95 and 96; 101 and 102; 106 and 107; 113 and 114; 118–121; 126 and 127; 129–132; 133 and 134; 137–139; 140–142; 154 and 155; 157–164; 165–169; 176–180; 185–190; 199–200; 205–206; 208–209; 211–212; 245–247; 262–264; and 289–290.

A number of problems (218, 219, 220, 221, 242, 273, 278, 279, 280, 285, 286 and 287) exemplify complexities arising from the presence of chiral centres, and some problems illustrate restricted rotation about amide bonds (191, 275 and 281). There are a number of problems dealing with the structures of compounds of biological, environmental or industrial significance (41, 49, 64, 91, 92, 93, 94, 98, 146, 151, 152, 160, 179, 180, 191, 198, 219, 225, 231, 235, 236, 269, 285, 277, 278, 279, 284, 286 and 287).

Problems 295–300 are again structures from spectra, but with the data presented in a textual form such as might be encountered when reading the experimental section of a paper or report.

Problems 301–309 deal with the use of NMR spectroscopy for quantitative analysis and for the analysis of mixtures of compounds.

In Chapter 9, there are also three worked solutions (to problems 117, 146 and 77) as an illustration of a logical approach to solving problems. However, with the exception that we insist that students perform all routine measurements first, we do not recommend a mechanical attitude to problem solving – intuition has an important place in solving structures from spectra as it has elsewhere in chemistry.

Bona fide instructors may obtain a list of solutions (at no charge) by writing to the authors or EMAIL: L.Field@unsw.edu.au

We wish to thank the many graduate students and research associates who, over the years, have supplied us with many of the compounds used in the problems.

L. D. Field

H. L. Li

A. M. Magill

January 2020

LIST OF TABLES

List of Tables

LIST OF FIGURES

1

INTRODUCTION

1.1 GENERAL PRINCIPLES OF ABSORPTION SPECTROSCOPY

Spectroscopy involves resolving electromagnetic radiation into its component wavelengths (or frequencies) and absorption spectroscopy is the absorption of electromagnetic radiation by matter as a function of wavelength.

In Organic Chemistry, we typically deal with molecular spectroscopy, *i.e.* the spectroscopy of atoms that are bound together in molecules rather than absorption by individual atoms or ions.

An absorption spectrum is a plot or graph of the absorption of energy (radiation) as a function of its wavelength (λ) or frequency (ν). A schematic absorption spectrum is given in Figure 1.1.

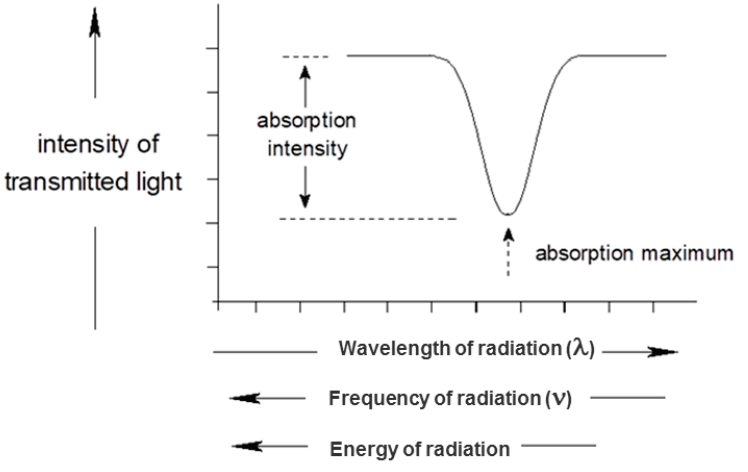


Figure 1.1 Schematic Absorption Spectrum

It follows that the *x*-axis in Figure 1.1 is an **energy** scale, since the frequency, wavelength and energy (E) of electromagnetic radiation are interrelated by the Planck–Einstein relation:

$$E = h.\nu$$
$$\text{and} \quad \nu.\lambda = c$$

where ν is the frequency of the electromagnetic radiation, λ is the wavelength of the electromagnetic radiation, and *c* is the velocity of light.

Organic Structures from Spectra, Sixth Edition, L. D. Field, H. L. Li and A. M. Magill
© 2020 John Wiley & Sons Ltd. Published 2020 by John Wiley & Sons Ltd.

An absorption band can be characterised primarily by two parameters:

(a) the wavelength (or frequency) at which maximum absorption occurs

(b) the intensity of absorption at this wavelength compared to base-line (or background) absorption

A spectroscopic transition takes a molecule from one energy state to a state of higher energy. For any spectroscopic transition between energy states (*e.g.* E_1 and E_2 in Figure 1.2), the change in energy (ΔE) is given by:

$$\Delta E = h\nu$$

where h is Planck's constant and ν is the frequency of the electromagnetic energy absorbed.

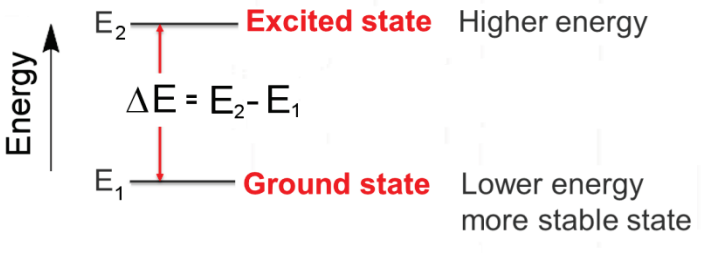


Figure 1.2 Definition of a Spectroscopic Transition

It follows that $\Delta E \propto \nu$ and that $\Delta E \propto 1/\lambda$; *i.e.* the larger ΔE, the *higher* the frequency of radiation required for absorption to take place or the *shorter* the wavelength of radiation required for absorption to take place.

The *y*-axis in Figure 1.1 measures the intensity of the absorption band and this depends on the number of molecules observed (the Beer–Lambert Law) and the probability of the transition between the energy levels.

A spectrum consists of distinct bands or transitions because the absorption (or emission) of energy is quantised. The energy gap for a transition (and hence the absorption frequency) is a ***molecular property*** and it is ***characteristic of molecular structure***. The absorption intensity is also a molecular property and both the frequency and the intensity of a transition can provide structural information.

1.2 CHROMOPHORES

In general, any spectral feature, *i.e.* a band or group of bands, is due not to the whole molecule, but to an identifiable part of the molecule, which we loosely call a *chromophore.*

A chromophore may correspond to a functional group (*e.g.* a hydroxyl group or the double bond in a carbonyl group). However, it may equally well correspond

to a single atom within a molecule or to a group of atoms (*e.g.* a methyl group) that is not normally associated with chemical functionality.

The detection of a chromophore permits us to deduce the presence of a *structural fragment* or a *structural element* in the molecule. The fact that it is the chromophores and not the molecule as a whole that give rise to spectral features is fortunate because it permits complete molecular structures to be built up piece-by-piece from the molecular fragments.

1.3 DEGREE OF UNSATURATION

Traditionally, the molecular formula of a compound was derived from elemental analysis and its molecular weight, and these were determined independently. The concept of the **degree of unsaturation** of an organic compound derives simply from the tetravalency of carbon. For a non-cyclic hydrocarbon (*i.e.* an alkane) the number of hydrogen atoms must be twice the number of carbon atoms plus two, any "deficiency" in the number of hydrogens must be due to the presence of unsaturation, *i.e.* double bonds, triple bonds or rings in the structure.

The degree of unsaturation can be calculated from the molecular formula for all compounds containing C, H, N, O, S or the halogens. There are three basic steps in calculating the degree of unsaturation:

Step 1 – take the molecular formula and replace all halogens by hydrogens

Step 2 – omit all of the sulfur or oxygen atoms

Step 3 – for each nitrogen, omit the nitrogen and omit one hydrogen

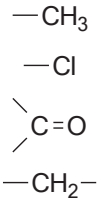
After these three steps, the molecular formula is reduced to C_nH_m and the degree of unsaturation is given by:

$$\text{Degree of Unsaturation} = n - \frac{m}{2} + 1$$

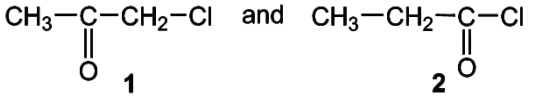
The degree of unsaturation indicates the number of π bonds or rings that the compound contains. For example, a compound whose molecular formula is $C_4H_9NO_2$ is reduced to C_4H_8, which gives a degree of unsaturation of 1. This indicates that the molecule must have one π bond or one ring. Note that a triple bond (*e.g.* the –C≡C– bond in an alkyne or the –C≡N bond in a nitrile) contributes two units of unsaturation (two π bonds). Note also that any compound that contains an aromatic ring always has a degree of unsaturation greater than or equal to 4, since the aromatic ring contains a ring plus three π bonds. Similarly, if a compound has a degree of unsaturation greater than or equal to 4, one should suspect the possibility that the structure contains an aromatic ring.

1.4 CONNECTIVITY

Even if it were possible to identify sufficient structural elements in a molecule to account for the molecular formula, it may not be possible to deduce the structural formula from a knowledge of the structural elements alone. For example, it could be demonstrated that a substance of molecular formula C_3H_5OCl contains the structural elements:



and this leaves two possible structures:



Not only the presence of various structural elements, but also their juxtaposition, must be determined to establish the structure of a molecule. Fortunately, spectroscopy often gives valuable information concerning the *connectivity* of structural elements and in the above example it would be very easy to determine whether there is a ketonic carbonyl group (as in **1**) or an acid chloride (as in **2**). In addition, it is possible to determine independently whether the methyl ($–CH_3$) and methylene ($–CH_2–$) groups are separated (as in **1**) or adjacent (as in **2**).

1.5 SENSITIVITY

Sensitivity is generally taken to signify the limits of detectability of a chromophore. Some methods (*e.g.* ^{1}H NMR spectroscopy) detect all chromophores accessible to them with equal sensitivity while in other techniques (*e.g.* UV spectroscopy) the range of sensitivity towards different chromophores spans many orders of magnitude. Mass spectroscopy is the most sensitive of the common spectroscopic techniques and requires only very small amounts of sample ($< 10^{-10}$ g) whereas ^{13}C NMR typically requires tens of milligrams of sample. In terms of overall sensitivity:

$$\text{MS} > \text{UV} > \text{IR} > {}^1\text{H NMR} > {}^{13}\text{C NMR}$$

but the relative sensitivity of different spectroscopic techniques often depends on the specific chromophores present in a molecule.

1.6 PRACTICAL CONSIDERATIONS

The five major spectroscopic methods (MS, UV, IR, ^{1}H NMR and ^{13}C NMR) have become established as the principal tools for the determination of the structures of organic compounds because, between them, they detect a wide variety of structural elements.

The instrumentation and skills involved in the use of all five major spectroscopic methods are now widely spread, but the ease of obtaining and interpreting the data from each method under real laboratory conditions varies.

In very general terms:

(a) While the ***cost*** of each type of instrumentation differs greatly (NMR instruments cost between $50,000 and several million dollars), as an overall guide, MS and NMR instruments are much more costly than UV and IR spectrometers. With increasing cost comes increasing difficulty in maintenance and the required operator expertise, thus compounding the total outlay.

(b) In terms of ***ease of usage*** for routine operation, most UV and IR instruments are comparatively straightforward bench-top laboratory instruments. NMR spectrometers are also common as "hands-on" instruments in most chemistry laboratories and the users require routine training and a degree of basic computer literacy. Similarly some mass spectrometers are now designed to be used by researchers as "hands-on" routine instruments. However, the more advanced NMR spectrometers and most mass spectrometers are still sophisticated instruments that are usually operated and maintained by specialists.

(c) The ***scope*** of each spectroscopic method can be defined as the amount of useful information it provides. This is a function of the total amount of information obtainable and also how difficult the data are to interpret. The scope of each method varies from problem to problem, and each method has its aficionados and specialists, but the overall utility undoubtedly decreases in the order:

$$\text{NMR} > \text{MS} > \text{IR} > \text{UV}$$

with the combination of ^{1}H and ^{13}C NMR spectroscopy providing the most useful information.

(d) The ***theoretical background*** needed for each method varies with the nature of the experiment, but the minimum overall amount of theory needed decreases in the order:

$$\text{NMR} >> \text{MS} > \text{UV} \approx \text{IR}$$

2

ULTRAVIOLET (UV) SPECTROSCOPY

2.1 THE NATURE OF ULTRAVIOLET SPECTROSCOPY

The term "UV spectroscopy" generally refers to the excitation of *electronic transitions* by absorption of energy in the ultraviolet region of the electromagnetic spectrum (λ in the range approximately 200−380 nm) accessible to standard UV spectrometers.

Electronic transitions are also responsible for absorption in the visible region of the spectrum (approximately 380–800 nm) which is easily accessible instrumentally but of less importance when solving structural problems because most organic compounds are colourless. An extensive region at wavelengths shorter than ~200 nm ("vacuum ultraviolet") also corresponds to electronic transitions, but this region is not readily accessible with standard instruments. UV spectra used for determination of structures are invariably obtained in solution.

2.2 BASIC INSTRUMENTATION

Basic instrumentation for both UV and IR spectroscopies consists of an energy *source*, a *dispersing device* (prism or grating), a *sample cell* and a *detector,* arranged as schematically shown in Figure 2.1.

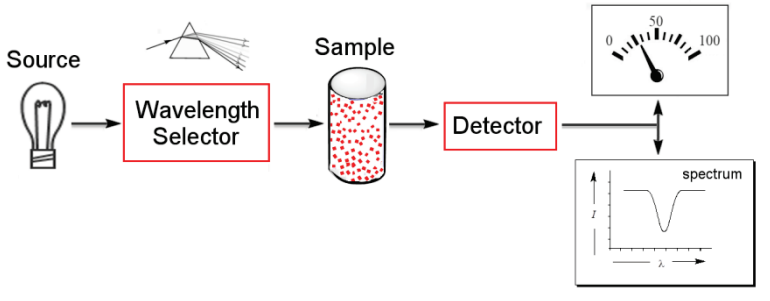


Figure 2.1 Schematic Representation of an IR or UV Spectrometer

The dispersing device scans through the range of wavelengths produced by the source and these pass through the sample. The drive of the dispersing device is synchronised with the *x*-axis of the recorder or fed directly to a computer, so that the *x*-axis tracks the wavelength of radiation reaching the detector. The signal

Organic Structures from Spectra, Sixth Edition, L. D. Field, H. L. Li and A. M. Magill
© 2020 John Wiley & Sons Ltd. Published 2020 by John Wiley & Sons Ltd.

from the detector is transmitted to the *y*-axis of the recorder or to a computer and this records how much radiation is absorbed by the sample at any particular wavelength.

In practice, almost all instruments are *double-beam* spectrometers and in this type of instrument, the beam is split and part of the beam goes through a *reference cell*, containing only solvent, and part of the beam goes through the sample. The absorbance of the reference cell is subtracted from the absorbance of the sample cell. Double-beam instruments eliminate any absorbance from the solvent and also cancel out absorption resulting from the atmosphere in the optical path (Figure 2.2).

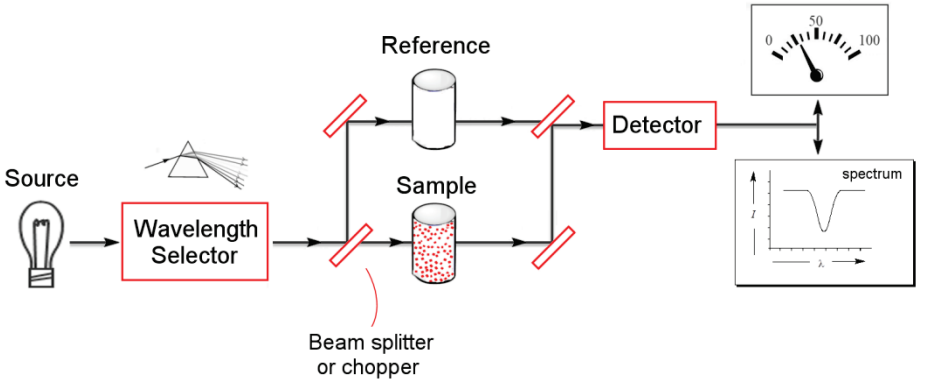


Figure 2.2 Schematic Representation of a Double-Beam Absorption Spectrometer

The energy source must be appropriate for the wavelengths of radiation being scanned. For UV spectroscopy the source is usually a deuterium lamp in which an electrical discharge through a lamp filled with deuterium gas produces a broad spectrum of light across the UV range in the electromagnetic spectrum.

The samples for UV spectroscopy are typically dissolved in solution and contained in small cells (cuvettes). The cells and optical components must be as transparent as possible to wavelengths being scanned and are typically made of quartz or fused silica. Note that conventional glass and most plastics absorb UV radiation very strongly so these materials are not used in cells for UV spectroscopy. Ethanol, hexane, water or dioxane are usually chosen as solvents as these have minimal absorption in the UV region of the spectrum.

2.3 QUANTITATIVE ASPECTS OF ULTRAVIOLET SPECTROSCOPY

The *y*-axis of a UV spectrum may be calibrated in terms of the intensity of transmitted light (*i.e.* the percentage of transmission or absorption) or it may be calibrated on a logarithmic scale, *i.e.* in terms of *absorbance* (A) (Figure 2.3).

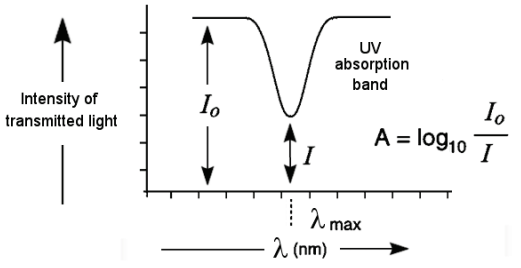


Figure 2.3 Definition of Absorbance (A)

Absorbance is proportional to concentration and path length (the Beer–Lambert Law). The intensity of absorption is usually expressed in terms of *molar absorbance* or the *molar extinction coefficient* (ε) given by:

$$\varepsilon = \frac{M\,A}{C\,l}$$

where M is the molecular weight, C the concentration (in grams per litre) and *l* is the path length through the sample in centimetres.

UV absorption bands (Figure 2.3) are characterised by the wavelength of the absorption maximum (λ_{max}) and ε. The values of ε associated with commonly encountered chromophores vary between 10 and 10^5. For convenience, extinction coefficients are usually tabulated as $\log_{10}(\varepsilon)$ as this gives numerical values that are easier to manage. The fact that some species may have very large extinction coefficients means that care must be taken in the preparation of samples because the presence of small amounts of strongly absorbing impurities may lead to errors in the interpretation of UV data.

2.4 CLASSIFICATION OF UV ABSORPTION BANDS

UV absorption bands have fine structure because of the presence of vibrational sub-levels, but this is rarely observed in solution due to collisional broadening. As the transitions are associated with changes of electron orbitals, they are often described in terms of the orbitals involved, *e.g.*

$\sigma \rightarrow \sigma^*$
$\pi \rightarrow \pi^*$
$n \rightarrow \pi^*$
$n \rightarrow \sigma^*$

where *n* denotes a non-bonding orbital, the asterisk denotes an antibonding orbital and σ and π have the usual meaning in terms of bonding categories.

Another method of classification uses the symbols:

B (for benzenoid)

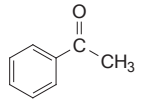
E (for ethylenic)

R (for radical-like)

K (for conjugated – from the German "konjugierte")

A molecule may give rise to more than one band in its UV spectrum, either because it contains more than one chromophore or because more than one transition of a single chromophore is observed. However, UV spectra typically contain far fewer features (bands) than IR, MS or NMR spectra and therefore have a lower information content. The ultraviolet spectrum of acetophenone in ethanol contains three easily observed bands (Table 2.1).

Table 2.1 Observable UV Absorption Bands for Acetophenone



acetophenone

λ_{max}(nm)	ε	$\log_{10}(\varepsilon)$	Assignment	
244	12,600	4.1	π → π*	K
280	1,600	3.2	π → π*	B
60	317	1.8	*n* → π*	R

2.5 SPECIAL TERMS IN UV SPECTROSCOPY

Auxochromes (auxiliary chromophores) are groups that have little UV absorption by themselves, but which often have significant effects on the absorption (both λ_{max} and ε) of a chromophore to which they are attached. Generally, auxochromes contain atoms with one or more lone pairs, *e.g.* –OH, −OR, $–NR_2$, –halogen.

If a structural change, such as the attachment of an auxochrome, leads to the absorption maximum being shifted to a longer wavelength, the phenomenon is termed a *bathochromic shift.* A shift towards shorter wavelength is called a *hypsochromic shift.*

2.6 IMPORTANT UV CHROMOPHORES

Most of the reliable and useful data are due to relatively strongly absorbing chromophores ($\varepsilon > 200$) that are mainly indicative of conjugated or aromatic systems. The examples listed below encompass most of the commonly encountered effects.

2.6.1 DIENES AND POLYENES

Extension of conjugation in a carbon chain is always associated with a pronounced shift towards longer wavelength, and usually towards greater absorption intensity (Table 2.2).

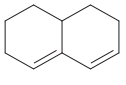
Table 2.2 The Effect of Extended Conjugation on UV Absorption

Alkene	λ_{max} (nm)	ε	$\log_{10}(\varepsilon)$
$CH_2=CH_2$	165	10,000	4.0
$CH_3–CH_2–CH=CH–CH_2–CH_3$ (*trans*)	184	10,000	4.0
$CH_2=CH–CH=CH_2$	217	20,000	4.3
$CH_3–CH=CH–CH=CH_2$ (*trans*)	224	23,000	4.4
$CH_2=CH–CH=CH–CH=CH_2$ (*trans*)	263	53,000	4.7
$CH_3–(CH=CH)_5–CH_3$ (*trans*)	341	126,000	5.1

When there are more than eight conjugated double bonds, the absorption maximum of polyenes is further shifted such that they absorb light strongly in the visible region of the spectrum.

There are empirical rules (Woodward's Rules) of good predictive value and these allow the estimation of the positions of the absorption maxima in conjugated alkenes and conjugated carbonyl compounds.

The stereochemistry and the presence of substituents also influence UV absorption by the diene chromophore. For example:



λ_{max} = 214 nm

ε = 16,000

$\log_{10}(\varepsilon)$ = 4.2

λ_{max} = 253 nm

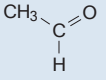
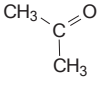
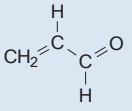
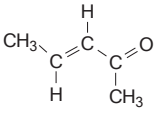
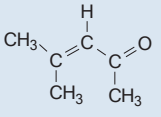
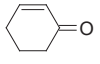
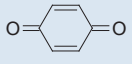
ε = 8,000

$\log_{10}(\varepsilon)$ = 3.9

2.6.2 CARBONYL COMPOUNDS

All carbonyl derivatives exhibit weak ($\varepsilon < 100$) absorption between 250 and 350 nm, and this is only of marginal use in determining structure. However, conjugated carbonyl derivatives always exhibit strong UV absorption (Table 2.3).

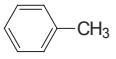
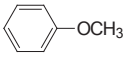
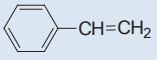
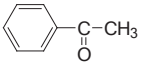
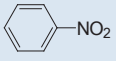
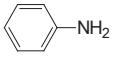
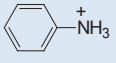
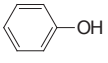
Table 2.3 UV Absorption Bands in Common Carbonyl Compounds

Compound	Structure	λ_{max} (nm)	ε	$\log_{10}(\varepsilon)$
Acetaldehyde		293 (hexane solution)	12	1.1
Acetone		279 (hexane solution)	15	1.2
Propenal		207 328 (ethanol solution)	12,000 20	4.1 1.3
(E)-Pent-3-en-2-one		221 312 (ethanol solution)	12,000 40	4.1 1.6
4-Methylpent-3-en-2-one		238 316 (ethanol solution)	12,000 60	4.1 1.8
Cyclohex-2-en-1-one		225	7,950	3.9
Benzoquinone		247 292 363	12,600 1,000 250	4.1 3.0 2.4

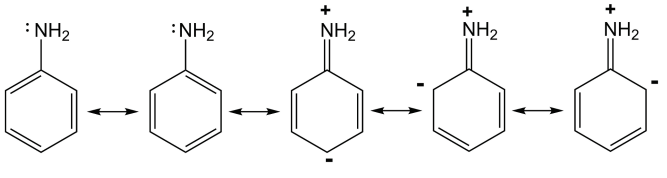
2.6.3 BENZENE DERIVATIVES

Benzene derivatives exhibit medium to strong absorption in the UV region. Bands usually have characteristic fine structure and the intensity of the absorption is strongly influenced by substituents. Examples listed in Table 2.4 include weak auxochromes ($-CH_3$, $-Cl$, $-OCH_3$), groups which increase conjugation ($-CH=CH_2$, $-C(=O)-R$, $-NO_2$) and auxochromes whose absorption is pH dependent ($-NH_2$ and $-OH$).

Table 2.4 UV Absorption Bands in Common Benzene Derivatives

Compound	Structure	λ_{max} (nm)	ε	$\log_{10}(\varepsilon)$
Benzene		184 204 256	60,000 7,900 200	4.8 3.9 2.3
Toluene		208 261	8,000 300	3.9 2.5
Chlorobenzene		216 265	8,000 240	3.9 2.4
Anisole		220 272	8,000 1,500	3.9 3.2
Styrene		244 282	12,000 450	4.1 2.7
Acetophenone		244 280	12,600 1,600	4.1 3.2
Nitrobenzene		251 280 330	9,000 1,000 130	4.0 3.0 2.1
Aniline		230 281	8,000 1,500	3.9 3.2
Anilinium ion		203 254	8,000 160	3.9 2.2
Phenol		211 270	6,300 1,500	3.8 3.2
Phenoxide ion		235 287	9,500 2,500	4.0 3.4

Aniline and phenoxide ion have strong UV absorptions resulting from the overlap of the lone pair on the nitrogen (or oxygen) with the π-system of the benzene ring. This may be visualised in the usual Valence Bond terms:



The striking changes in the ultraviolet spectra accompanying protonation of aniline and phenoxide ion are because of the loss (or substantial reduction) of the overlap between the lone pairs and the benzene ring.