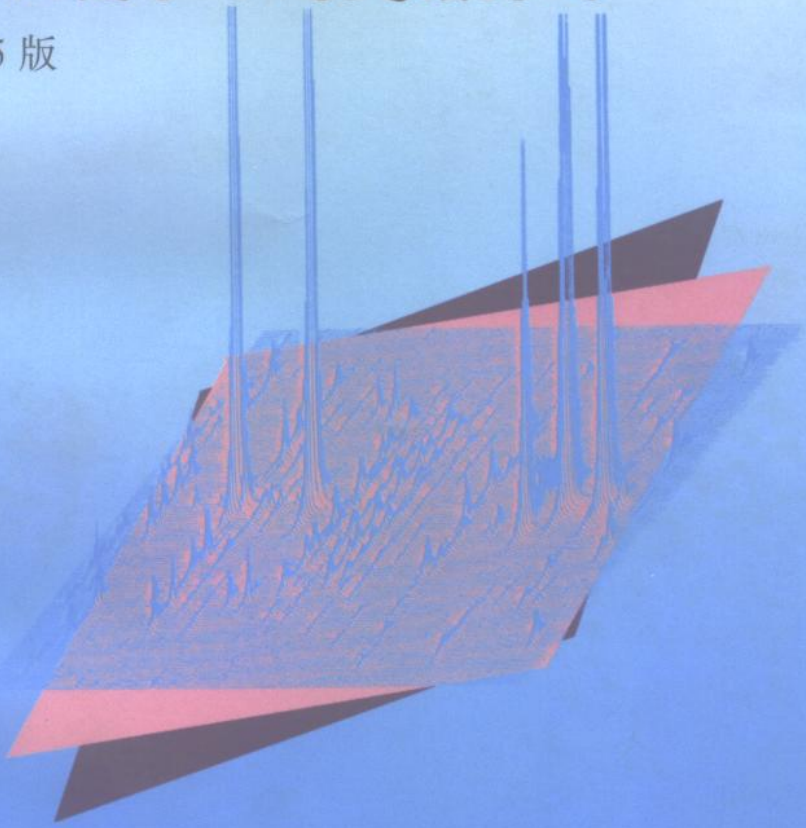
FIFTH EDITION

Spectroscopic Methods in Organic Chemistry

D. H. Williams I. Fleming

有机化学中的光谱方法

第 5 版



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Spectroscopic methods in organic chemistry
Fifth Edition

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书　　名：Spectroscopic Methods in Organic Chemistry　5th ed.
作　　者：D.H. Williams & I. Fleming
中 译 名：有机化学中的光谱方法　第 5 版
出 版 者：世界图书出版公司北京公司
印 刷 者：北京中西印刷厂
发　　行：世界图书出版公司北京公司（北京市朝阳门内大街 137 号　100010）
开　　本：1/32　850 × 1168　　印　张：10.75
版　　次：1998 年 12 月第 1 版　1998 年 12 月第 1 次印刷
书　　号：7-5062-4097-1/ O•233
版权登记：图字 01-98-2422
定　　价：54.00 元

世界图书出版公司北京公司已获得 McGraw-Hill Book Co. Singapore 授权在中国境内独家重印发行。

Published by
McGraw-Hill Publishing Company
Shoppenhangers Road · Maidenhead · Berkshire · SL6 2QL · England
Telephone 01628 23432
Fax 01628 770224

British Library Cataloguing in Publication Data
Williams, Dudley H.
Spectroscopic methods in organic
chemistry. — 5th ed.
I. Title II. Fleming, Ian
547.30858
ISBN 0-07-709147-7

Library of Congress Cataloging-in-Publication Data
Williams, Dudley H.
Spectroscopic methods in organic
chemistry/Dudley H. Williams, Ian Fleming. — 5th ed.
p. cm.
Includes bibliographical references and index.
ISBN 0-07-709147-7 (pbk. alk. paper)
1. Chemistry, Organic. 2. Spectrum analysis.
I. Fleming, Ian, . II. Title.
QD272.S6W54 1995
547.3'0858–dc20 95–14474
CIP

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IE ISBN: 0-07-116852-4

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Foreword

Spectroscopy is the cornerstone of the organic chemistry of the second half of the twentieth century. The introduction of ultraviolet spectroscopy (UV) in the 1930s and infrared spectroscopy (IR) in the 1940s provided chemists with effective methods for the recognition of functionality in organic molecules. For the first time, structural information could be obtained by small-scale, non-destructive experiments. The revolution continued with the introduction of mass spectrometry (MS) in the 1950s. This experiment provided the molecular formula for a compound, and gave an insight into structure from the fragmentation pattern.

However, the analytical method that has had the greatest impact on science has been nuclear magnetic resonance spectroscopy (NMR). The effect of NMR has come in three distinct waves. Although the first applications in organic chemistry came in the 1950s, the tool was not widely used until the advent of the Varian Associates A-60 spectrometer in the early 1960s. The new experiment provided the final piece of the structural puzzle in many cases; UV and IR gave the functionality, MS gave the formula, and NMR and MS together allowed one to put together the molecular skeleton. The effect on organic chemistry was immediate and electrifying; by the end of that decade, virtually every publication dealing with organic chemistry included NMR data as the most important structural evidence. The pace of progress in structure determination increased perceptibly.

A second identifiable stage in the introduction of NMR into structural chemistry resulted from application of the Fourier transform (FT) method to the nuclear magnetic resonance experiment. The development of the FT instrument in the 1970s had an effect on organic chemistry and biological chemistry almost as far-reaching as the initial introduction of proton NMR a decade earlier. The application of the FT technique to proton NMR allowed the use of this important method with surprisingly small samples. It also solved the dual problems of the low natural abundance and relatively small magnetic sensitivity of carbon-13, and allowed the NMR experiment to be applied to this isotope. With carbon-13 NMR (CMR) the chemist could look directly at the carbon backbone of molecules, when CMR was used in combination with proton NMR and the new separation techniques (gas chromatography, thin-layer chromatography, high performance liquid chromatography) structural elucidation took on new dimensions.

The third surge of activity has come in the present decade, and is a daughter of the computer revolution. 'Two-dimensional' (2D) NMR is a still-burgeoning aspect of the method that may influence the way chemists think about structure determination more than any of the earlier spectroscopic techniques. With this powerful family of experiments, one may correlate proton and carbon spectra, trace the connectivity of a molecular skeleton, and even determine non-bonded distances within molecules and between different molecules. 2D NMR now permits the kind

of detailed structural 'photograph' that can also be obtained in the crystalline state by the technique of X-ray crystallography.

This book, the Fifth Edition of a classic work on spectroscopy, concentrates on the practical aspect of *using* spectroscopic techniques to solve structural problems. It is written at a level that is suitable for an advanced undergraduate or graduate course in applied spectroscopy, but will also give practising chemists a valuable overview of the subject, as well as a good introduction to new techniques (2D NMR and recently introduced methods of producing ions for mass spectrometry). It is a resource that should be on the desks of *all* graduate students beginning organic chemistry, and could be read with profit by many of their professors as well.

Clayton H. Heathcock
Berkeley
January 1995

Preface

We have written this book as a guide to the interpretation of the ultraviolet, infrared, nuclear magnetic resonance and mass spectra of organic compounds; it is intended both as a textbook suitable for a first course in the subject and as a handbook for practising organic chemists.

Spectroscopic methods are now used at some point in the solution of almost all problems in organic chemistry. Three of these methods rely on the selective absorption of electromagnetic radiation by organic molecules. The first method, ultraviolet spectroscopy, is used to detect conjugated systems, because the promotion of electrons from the ground state to the excited state of such systems gives rise to absorption in this region. The second, infrared spectroscopy, is used to detect and identify the vibrations of molecules, and especially the characteristic vibrations of the double and triple bonds present in many functional groups. The third method, nuclear magnetic resonance spectroscopy, uses a longer wavelength of the electromagnetic spectrum to detect changes in the alignment of nuclear magnets in strong magnetic fields. Absorption is observed from such nuclei as ^{1}H, ^{13}C, ^{15}N, ^{19}F, and ^{31}P; and the precise frequency of absorption is a very sensitive measure of the magnetic, and hence the chemical, environment of such nuclei. Moreover, the number and disposition of neighbouring magnetic nuclei influence the appearance of that absorption in a well-defined way. The result, particularly with the ubiquitous hydrogen and ^{13}C nuclei, is a considerable gain in information about the arrangement of functional groups and hydrocarbon residues in a molecule. The fourth method, mass spectrometry, measures the mass-to-charge ratio of organic ions. Structural information comes from the moderately predictable fragmentation organic molecules undergo; the masses of the fragment ions can often be related to likely structures.

Other regions of the electromagnetic spectrum are often used to determine the structure of organic molecules. X-ray diffraction can be used to pinpoint centres of high electron density (i.e. the atoms). Microwave absorption is used to measure molecular rotations. Electron spin resonance, also using radio-frequency signals, detects unpaired electrons, and can be used to measure the distribution of electron density in radicals. Optical rotatory dispersion and circular dichroism, using visible and ultraviolet light, measure the change in rotatory power of molecules, as the wavelength of the polarized light is changed; such measurements can often be related to the absolute configuration of molecules. Other physical methods, such as the measurement of p*K*s, reaction rates, and dipole moments, are also used by organic chemists for structure determination. But all of these methods are more specialized than the four spectroscopic methods described in this book: these four methods are so regularly used that all organic chemists need to know about them.

We have kept discussion of the theoretical background to a minimum, since correlations between spectra and structure can successfully be made without

detailed theoretical knowledge; this aspect of the subject has, moreover, been covered in many books, including the book by C. N. Banwell and E. McCash, *Fundamentals of Molecular Spectroscopy*, Fourth Edition. We have instead discussed in each chapter the kind of information given by each of the four spectroscopic methods, and we have described how to read each kind of spectrum to get that information out of it. We have included in each chapter tables of values: UV maxima, IR frequencies, NMR chemical shifts and coupling constants, and common mass fragments found in mass spectra—all of which are regularly needed for the day-to-day interpretation of spectra.

Finally, in Chapter 5, we give examples of the way in which the spectroscopic methods can be brought together to solve fairly simple structural problems. There are then 27 problems at the end of the chapter. These are intended to supplement an organized course which the student is attending. Throughout the book we have stressed the application of spectroscopic methods to structure determination, though the application to other problems is limited only by the ingenuity of the researcher and analyst.

Ian Fleming
Dudley H. Williams
Cambridge

Preface to Fifth Edition

In preparing a Fifth Edition, we have considerably extended the coverage of two-dimensional NMR and introduced for the first time in the book the powerful techniques of TOCSY and long-range ^{1}H–^{13}C COSY (Chapter 3). In the chapter on mass spectrometry (Chapter 4), we have introduced the new methods of electrospray ionization (ESI) and matrix-assisted laser desorption (MALDI), and illustrated how these methods, when coupled with ion analysis in quadrupole, Fourier transform ion-cyclotron resonance (FT–ICR), or time-of-flight (TOF) instruments can be used to determine the molecular weights of very large and highly polar molecules.

Although the above approach extends the coverage of the book from the traditional confines of classical organic chemistry into biochemistry, we have thought this desirable for several reasons. First, as the power of NMR and mass spectrometry has increased during the last 20 years, these methods have naturally been applied to larger and larger molecules, and it seems desirable to cover the (often common) principles and methods used for both small and large molecules within the confines of one book. Second, the traditional boundaries between the various scientific disciplines have in any case become increasingly blurred during the last decade (and from the viewpoint of education, this seems to be a good thing). Third, our book is intended not only as a textbook for undergraduates but also as a data source, and a book covering principles and methods, for those in industry (e.g. pharmaceuticals, toxicology, agrochemicals, etc.). These individuals are often required to handle the whole range of molecules.

In Chapter 5, we have increased the number of worked examples and greatly increased the number of problems in order to give both students and current practitioners a chance to hone their skills. Many of the NMR spectra in Chapter 5 were run by Derek Pert at Bruker Spectrospin Ltd, UK, to whom we are especially grateful. We also thank the following for permission to reproduce figures: Dr James McAlpine and *J. Antibiotics* for Fig. 3.44, Dr Clive Pierce for Fig. 3.48, Prof. H. Seto and *J. Antibiotics* for Fig. 3.49, Prof. Y. Yamada and *J. Antibiotics* for Figs 3.51 and 3.52, Dr H. Oschkinat for Fig. 3.55, Dr Richard Smith and *Analytical Chemistry* for Fig. 4.33, Prof. Fred W. McLafferty for Fig. 4.34, Prof. Franz Hillenkamp and *Analytical Chemistry* for Fig. 4.35, Prof. Jack Henion and *Analytical Chemistry* for Figs 4.38, 4.39, and 4.40, and Dr Robert Dancer for Example 5 in Chapter 5.

Dudley H. Williams
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Cambridge

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1. Ultraviolet and visible spectra

1.1 Introduction

The visible and ultraviolet spectra of organic compounds are associated with transitions between electronic energy levels. The transitions are generally between a bonding or lone-pair orbital and an unfilled non-bonding or anti-bonding orbital. The wavelength of the absorption is then a measure of the separation of the energy levels of the orbitals concerned. The highest energy separation is found when electrons in σ-bonds are excited, giving rise to absorption in the 120–200 nm ($1\,\text{nm} = 10^{-7}\,\text{cm} = 10\,\text{Å} = 1\,\text{m}\mu$) range. This range, known as the vacuum ultraviolet, since air must be excluded from the instrument, is both difficult to measure and relatively uninformative. Above 200 nm, however, excitation of electrons from p- and d-orbitals and π-orbitals, and, particularly, π-conjugated systems, gives rise to readily measured and informative spectra.

1.2 The energy of electronic excitation

The energy is related to wavelength by Eq. 1.1.

$$E(\text{kJ mol}^{-1}) = \frac{1.19 \times 10^5}{\lambda(\text{nm})} \tag{1.1}$$

Thus 297 nm, for example, is equivalent to 400 kJ ($\approx$ 96 kcal)—enough energy, incidentally, to initiate many interesting reactions; compounds should not, therefore, be left in the ultraviolet beam any longer than is necessary.

1.3 The absorption laws

Two empirical laws have been formulated about the absorption intensity. *Lambert's law* states that the fraction of the incident light absorbed is independent of the intensity of the source. *Beer's law* states that the absorption is proportional to the number of absorbing molecules. From these laws, the remaining variables give the Eq. 1.2.

$$\log_{10} \frac{I_0}{I} = \varepsilon.l.c \tag{1.2}$$

I_0 and I are the intensities of the incident and transmitted light respectively, l is the path length of the absorbing solution in centimetres, and c is the concentration in moles per litre. $\text{Log}_{10}\,(I_0/I)$ is called the absorbance or optical density; ε is known as the molar extinction coefficient and has units of $1000\,\text{cm}^2\,\text{mol}^{-1}$ but the units are, by convention, never expressed.

1.4 Measurement of the spectrum

The ultraviolet or visible spectrum is usually taken of a very dilute solution. An appropriate quantity of the compound (often about 1 mg when the compound has a molecular weight of 100–200) is weighed accurately, dissolved in the solvent of choice (see below), and made up to, for instance, 100 ml. A portion of this is transferred to a silica cell. The cell is so made that the beam of light passes through a 1 cm thickness (the value l in Eq. 1.2) of solution. A matched cell containing pure solvent is also prepared, and each cell is placed in the appropriate place in the spectrometer. This is so arranged that two equal beams of ultraviolet or visible light are passed, one through the solution of the sample, one through the pure solvent. The intensities of the transmitted beams are then compared over the whole wavelength range of the instrument. In most spectrometers there are two sources, one of 'white' ultraviolet and one of white visible light, which have to be changed when a complete scan is required. Usually either the visible or ultraviolet alone is sufficient for the purpose in hand. The spectrum is plotted automatically on most machines as a $\log_{10}(I_0/I)$ ordinate and λ abscissa. For publication and comparisons these are often converted to an ε versus λ or log ε versus λ plot. The unit of λ is almost always nm. Strictly speaking, the intensity of a transition is better measured by the area under the absorption peak (when plotted as ε versus frequency) than by the intensity of the maximum of the peak. For several reasons, most particularly convenience and the difficulty of dealing with overlapping bands, the latter procedure is adopted in everyday use. Spectra are quoted, therefore, in terms of λ_{max}, the wavelength of the absorption peak, and ε_{max}, the intensity of the absorption peak as defined by Eq. 1.2.

1.5 Vibrational fine structure

The excitation of electrons is accompanied by changes in the vibrational and rotational quantum numbers so that what would otherwise be an absorption *line* becomes a broad peak containing vibrational and rotational fine structure. Due to interactions of solute with solvent molecules this is usually blurred out, and a smooth curve is observed. In the vapour phase, in non-polar solvents, and with certain peaks (e.g. benzene with the 260 nm band), the vibrational fine structure is sometimes observed.

1.6 Choice of solvent

The solvent most commonly used is 95 per cent ethanol (commercial absolute ethanol contains residual benzene which absorbs in the ultraviolet). It is cheap, a good solvent, and transparent down to about 210 nm. Fine structure, if desired, may be revealed by using cyclohexane or other hydrocarbon solvents which, being less polar, have least interaction with the absorbing molecules. Table 1.1 gives a list of common solvents and the minimum wavelength from which they may be used in 1 cm cells.

Table 1.1 Some solvents used in ultraviolet spectroscopy

Solvent	*Minimum wavelength for 1 cm cell, nm*
Acetonitrile	190
Water	191
Cyclohexane	195
Hexane	201
Methanol	203
Ethanol	204
Ether	215
Methylene dichloride	220
Chloroform	237
Carbon tetrachloride	257

The effect of solvent polarity on the position of maxima is discussed in Sec. 1.9.

1.7 Selection rules and intensity

The irradiation of organic compounds may or may not give rise to excitation of electrons from one orbital (usually a lone-pair or bonding orbital) to another orbital (usually a non-bonding or anti-bonding orbital). It can be shown that:

$$\varepsilon = 0.87 \times 10^{-20} P.\mathbf{a} \tag{1.3}$$

where P is called the transition probability (with values from 0 to 1) and **a** is the target area of the absorbing system: the absorbing system is usually called a chromophore. With common chromophores of the order of 10 Å long, a transition of unit probability will have an ε value of 10^5. This is close to the highest observed values, though—with unusually long chromophores—values in excess of this have been measured. In practice, a chromophore giving rise to absorption by a fully allowed transition will have ε values greater than about 10 000, while those with low transition probabilities will have ε values below 1000. The important point is that, in general, *the longer a particular kind of chromophore, the more intense the absorption.*

There are many factors that affect the transition probability of any particular transition. In the first place there are rules about which transitions are allowed and which are forbidden. These are complicated because they are a function of the symmetry and multiplicity both of the ground state and excited state orbitals concerned. The spectra of chromophores, with ε_{max} less than about 10 000, are the result of 'forbidden' transitions. Two very important and 'forbidden' transitions are observed: the $n \rightarrow \pi^*$ band near 300 nm of ketones, with ε values of the order of 10 to 100; and the benzene 260 nm band and its equivalent in more complicated systems, with ε values from 100 upwards. Both occur because the symmetry which makes absorption strictly forbidden is broken up by molecular vibrations and—in the latter case—by substitution. Both types are discussed further under the sections on ketones and aromatic systems..

In this and the following discussions a very simplified theoretical picture is given; there is considerable danger in being satisfied with so little in so well developed a subject. The books by Jaffé and Orchin and by Murrell, listed in the bibliography, give excellent accounts.

1.8 Chromophores

The word chromophore is used to describe the system containing the electrons responsible for the absorption in question. Most of the simple unconjugated chromophores described in Table 1.2 give rise to such high-energy, and therefore such short-wavelength, absorption that they are of little use.

Table 1.2 The absorption of simple unconjugated chromophores

Chromophore	*Transition notation*†	λ_{max}, *nm*
σ-bonded electrons		
C—C and C—H	$\sigma \rightarrow \sigma^*$	~150
Lone-pair electrons		
—Ö—	$n \rightarrow \sigma^*$	~185
—N̈	$n \rightarrow \sigma^*$	~195
—S̈—	$n \rightarrow \sigma^*$	~195
C=Ö	$n \rightarrow \pi^*$	~300
C=Ö	$n \rightarrow \sigma^*$	~190
π-bonded electrons		
C=C (isolated)	$\pi \rightarrow \pi^*$	~190

† There are many other notations used.

One of the few useful simple unconjugated chromophores is the very weak forbidden $n \rightarrow \pi^*$ transition of ketones mentioned earlier which appears in the 300 nm region and is of particular importance in connection with optical rotatory dispersion. This band is due to the excitation of one of the lone pair of electrons (designated n) on the oxygen atom to the lowest anti-bonding orbital (designated π^*) of the carbonyl group. It is discussed further in the sections on solvent effects and on ketones.

The important chromophores are those in which conjugation is present. An isolated double bond or lone pair of electrons gives rise to a strong absorption maximum at about 190 nm, corresponding to the transition x in Fig. 1.1, at too short a wavelength for convenient measurement. When the molecular orbitals of two isolated double bonds are brought into conjugation, the energy level of the highest occupied orbital is raised and that of the lowest unoccupied anti-bonding orbital lowered (Fig. 1.1).

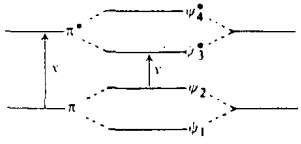

Fig. 1.1

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