

Organic Structures from Spectra

SIXTH EDITION

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WILEY

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CONTENTS

PREFACE	ix
LIST OF TABLES	xiii
LIST OF FIGURES	xv
1 INTRODUCTION	1
1.1 GENERAL PRINCIPLES OF ABSORPTION SPECTROSCOPY	1
1.2 CHROMOPHORES	2
1.3 DEGREE OF UNSATURATION	3
1.4 CONNECTIVITY	4
1.5 SENSITIVITY	4
1.6 PRACTICAL CONSIDERATIONS	5
2 ULTRAVIOLET (UV) SPECTROSCOPY	6
2.1 THE NATURE OF ULTRAVIOLET SPECTROSCOPY	6
2.2 BASIC INSTRUMENTATION	6
2.3 QUANTITATIVE ASPECTS OF ULTRAVIOLET SPECTROSCOPY	8
2.4 CLASSIFICATION OF UV ABSORPTION BANDS	8
2.5 SPECIAL TERMS IN ULTRAVIOLET SPECTROSCOPY	9
2.6 IMPORTANT UV CHROMOPHORES	10
2.6.1 DIENES AND POLYENES	10
2.6.2 CARBONYL COMPOUNDS	11
2.6.3 BENZENE DERIVATIVES	11
2.7 THE EFFECT OF SOLVENTS	13
3 INFRARED (IR) SPECTROSCOPY	14
3.1 ABSORPTION RANGE AND THE NATURE OF IR ABSORPTION	14
3.2 EXPERIMENTAL ASPECTS OF INFRARED SPECTROSCOPY	15
3.3 GENERAL FEATURES OF INFRARED SPECTRA	16
3.4 IMPORTANT IR CHROMOPHORES	18
3.4.1 -O-H AND -N-H STRETCHING VIBRATIONS	18
3.4.2 C-H STRETCHING VIBRATIONS	18
3.4.3 -C≡N AND -C≡C- STRETCHING VIBRATIONS	19
3.4.4 CARBONYL GROUPS	19
3.4.5 OTHER POLAR FUNCTIONAL GROUPS	21
3.4.6 THE FINGERPRINT REGION	21
4 MASS SPECTROMETRY	23
4.1 IONISATION PROCESSES	23
4.2 INSTRUMENTATION	25
4.3 MASS SPECTRAL DATA	26
4.3.1 HIGH RESOLUTION MASS SPECTRA	26
4.3.2 MOLECULAR FRAGMENTATION	28
4.3.3 ISOTOPE RATIOS	29

4.3.4	CHROMATOGRAPHY COUPLED WITH MASS SPECTROMETRY	31
4.3.5	METASTABLE PEAKS	31
4.4	REPRESENTATION OF FRAGMENTATION PROCESSES	31
4.5	FACTORS GOVERNING FRAGMENTATION PROCESSES	32
4.6	EXAMPLES OF COMMON TYPES OF FRAGMENTATION	32
4.6.1	CLEAVAGE AT BRANCH POINTS	32
4.6.2	β -CLEAVAGE	33
4.6.3	CLEAVAGE α TO CARBONYL GROUPS	33
4.6.4	CLEAVAGE α TO HETEROATOMS	34
4.6.5	RETRO DIELS–ALDER REACTION	34
4.6.6	THE McLAFFERTY REARRANGEMENT	34
5	¹ H NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY	36
5.1	THE PHYSICS OF NUCLEAR SPINS AND NMR INSTRUMENTS	36
5.1.1	THE LARMOR EQUATION AND NUCLEAR MAGNETIC RESONANCE	36
5.2	BASIC NMR INSTRUMENTATION	39
5.2.1	CW AND PULSED NMR SPECTROMETERS	39
5.2.2	NUCLEAR RELAXATION	42
5.2.3	MAGNETS FOR NMR SPECTROSCOPY	43
5.2.4	THE NMR SPECTRUM	44
5.3	CHEMICAL SHIFT IN ¹ H NMR SPECTROSCOPY	45
5.4	SPIN–SPIN COUPLING IN ¹ H NMR SPECTROSCOPY	52
5.4.1	SIGNAL MULTIPLICITY – THE N+1 RULE	54
5.5	ANALYSIS OF ¹ H NMR SPECTRA	55
5.5.1	SPIN SYSTEMS	56
5.5.2	STRONGLY AND WEAKLY COUPLED SPIN SYSTEMS	56
5.5.3	MAGNETIC EQUIVALENCE	58
5.5.4	CONVENTIONS FOR NAMING SPIN SYSTEMS	59
5.5.5	SPECTRAL ANALYSIS OF FIRST-ORDER NMR SPECTRA	60
5.5.6	SPLITTING DIAGRAMS	61
5.5.7	SPIN DECOUPLING	64
5.6	CORRELATION OF ¹ H– ¹ H COUPLING WITH STRUCTURE	65
5.6.1	NON-AROMATIC SPIN SYSTEMS	65
5.6.2	AROMATIC SPIN SYSTEMS	66
5.7	THE NUCLEAR OVERHAUSER EFFECT (NOE)	69
5.8	LABILE AND EXCHANGEABLE PROTONS	70
6	¹³ C NMR SPECTROSCOPY	72
6.1	COUPLING AND DECOUPLING IN ¹³ C NMR SPECTRA	72
6.2	THE NUCLEAR OVERHAUSER EFFECT (NOE) IN ¹³ C NMR SPECTROSCOPY	73
6.3	DETERMINING ¹³ C SIGNAL MULTIPLICITY USING DEPT	73
6.4	SHIELDING AND CHARACTERISTIC CHEMICAL SHIFTS IN ¹³ C NMR SPECTRA	76

7	2-DIMENSIONAL NMR SPECTROSCOPY	82
7.1	PROTON-PROTON INTERACTIONS BY 2D NMR	85
7.1.1	<i>COSY (CORRELATION SPECTROSCOPY)</i>	85
7.1.2	<i>TOCSY (TOTAL CORRELATION SPECTROSCOPY)</i>	86
7.1.3	<i>NOESY (NUCLEAR OVERHAUSER EFFECT SPECTROSCOPY)</i>	88
7.2	PROTON-CARBON INTERACTIONS BY 2D NMR	89
7.2.1	<i>THE HSQC (HETERONUCLEAR SINGLE QUANTUM CORRELATION) OR HSC (HETERONUCLEAR SHIFT CORRELATION) SPECTRUM</i>	89
7.2.2	<i>HMBC (HETERONUCLEAR MULTIPLE BOND CORRELATION)</i>	91
8	MISCELLANEOUS TOPICS	96
8.1	SOLVENTS FOR NMR SPECTROSCOPY	96
8.2	SOLVENT-INDUCED SHIFTS	97
8.3	DYNAMIC PROCESSES IN NMR – THE NMR TIME-SCALE	98
8.3.1	<i>CONFORMATIONAL EXCHANGE PROCESSES</i>	99
8.3.2	<i>INTERMOLECULAR EXCHANGE OF LABILE PROTONS</i>	99
8.3.3	<i>ROTATION ABOUT PARTIAL DOUBLE BONDS</i>	100
8.4	THE EFFECT OF CHIRALITY	100
8.5	THE NMR SPECTRA OF “OTHER NUCLEI”	101
9	DETERMINING THE STRUCTURE OF ORGANIC COMPOUNDS FROM SPECTRA	102
9.1	SOLVING PROBLEMS	103
9.2	WORKED EXAMPLES	104
10	PROBLEMS	115
	INDEX	538

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.

Preface

- (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.

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January 2020

LIST OF TABLES

Table 2.1	Observable UV Absorption Bands for Acetophenone	9
Table 2.2	The Effect of Extended Conjugation on UV Absorption	10
Table 2.3	UV Absorption Bands in Common Carbonyl Compounds	11
Table 2.4	UV Absorption Bands in Common Benzene Derivatives	12
Table 3.1	IR Absorption Frequencies for Common Organic Functional Groups	17
Table 3.2	C–H IR Absorption Frequencies in Common Functional Groups	19
Table 3.3	C≡N and C≡C Absorption Frequencies in Common Functional Groups	19
Table 3.4	C=O IR Absorption Frequencies in Common Functional Groups	20
Table 3.5	Characteristic IR Absorption Frequencies for Functional Groups	22
Table 4.1	Accurate Masses of Selected Isotopes	27
Table 4.2	Common Fragments and their Masses	29
Table 5.1	Nuclear Spins and Magnetogyric Ratios for Common NMR-Active Nuclei	38
Table 5.2	Resonance Frequencies of ^1H and ^{13}C Nuclei in Magnetic Fields of Different Strengths	39
Table 5.3	Typical ^1H Chemical Shift Values (δ) in Selected Organic Compounds	46
Table 5.4	Typical ^1H Chemical Shift Values (δ) of Selected Protons	47
Table 5.5	^1H Chemical Shift Values (δ) for Protons in Common Alkyl Derivatives	47
Table 5.6	Approximate ^1H Chemical Shift Ranges (δ) for Protons in Organic Compounds	48
Table 5.7	Approximate ^1H Chemical Shifts (δ) for Olefinic Protons	49
Table 5.8	Approximate ^1H Chemical Shifts (δ) for Aromatic Protons in Benzene Derivatives Ph–X in ppm Relative to Benzene at δ 7.26 ppm	50
Table 5.9	^1H Chemical Shifts (δ) for Protons in some Polynuclear Aromatic Compounds and Heteroaromatic Compounds	50
Table 5.10	Typical ^1H – ^1H Coupling Constants	53
Table 5.11	Relative Line Intensities for Simple Multiplets	54
Table 5.12	Proton–Proton Coupling Constants in Aromatic and Heteroaromatic Rings	67

List of Tables

Table 6.1	The Number of Aromatic ^{13}C Resonances in Benzenes with Different Substitution Patterns	75
Table 6.2	Typical ^{13}C Chemical Shift Values in Selected Organic Compounds	76
Table 6.3	Typical ^{13}C Chemical Shift Ranges in Organic Compounds	77
Table 6.4	Approximate ^{13}C Chemical Shift Ranges (δ) for Carbons in Organic Compounds	78
Table 6.5	^{13}C Chemical Shifts (δ) for sp^3 -hybridised Carbons in Alkyl Derivatives	79
Table 6.6	^{13}C Chemical Shifts (δ) for sp^2 -hybridised Carbons in Vinyl Derivatives $\text{CH}_2=\text{CH}-\text{X}$	79
Table 6.7	^{13}C Chemical Shifts (δ) for sp -hybridised Carbons in Alkynes: $\text{X}-\text{C}\equiv\text{C}-\text{Y}$	80
Table 6.8	Approximate ^{13}C Chemical Shifts (δ) for Aromatic Carbons in Benzene Derivatives $\text{Ph}-\text{X}$ in ppm Relative to Benzene at δ 128.5 ppm	80
Table 6.9	Characteristic ^{13}C Chemical Shifts (δ) in some Polynuclear Aromatic Compounds and Heteroaromatic Compounds	81
Table 8.1	^1H and ^{13}C Chemical Shifts for Common NMR Solvents	97

LIST OF FIGURES

Figure 1.1	Schematic Absorption Spectrum	1
Figure 1.2	Definition of a Spectroscopic Transition	2
Figure 2.1	Schematic Representation of an IR or UV Spectrometer	6
Figure 2.2	Schematic Representation of a Double-Beam Absorption Spectrometer	7
Figure 2.3	Definition of Absorbance (A)	8
Figure 4.1	Schematic Mass Spectrum	24
Figure 4.2	Schematic Diagram of an Electron-Impact Magnetic Sector Mass Spectrometer	26
Figure 4.3	Relative Intensities of the Cluster of Molecular Ions for Molecules Containing Combinations of Bromine and Chlorine Atoms	30
Figure 5.1	A Spinning Positive Charge Generates a Magnetic Field and Behaves Like a Small Magnet	36
Figure 5.2	Schematic Representation of a CW NMR Spectrometer	40
Figure 5.3	Schematic Representation of a Pulsed NMR Spectrometer	40
Figure 5.4	^1H NMR Spectra: (a) Time Domain Spectrum (FID); (b) Frequency Domain Spectrum Obtained after Fourier Transformation of (a)	41
Figure 5.5	^1H NMR Spectrum of Bromoethane (400 MHz, CDCl_3)	44
Figure 5.6	Shielding/deshielding Zones for Common Non-aromatic Functional Groups	52
Figure 5.7	^1H NMR Spectrum of Bromoethane (400 MHz, CDCl_3) Showing the Multiplicity of the Two ^1H Signals	54
Figure 5.8	Characteristic Multiplet Patterns for Common Organic Fragments	55
Figure 5.9	Aromatic Region of the ^1H NMR Spectrum of 2-Bromotoluene (acetone- d_6 solution) in Three Different Magnetic Field Strengths	57
Figure 5.10	Simulated ^1H NMR Spectra of a 2-Spin System as the Ratio $\Delta\nu/J$ is Systematically Decreased from 10.0 to 0.0	58
Figure 5.11	A Portion of the ^1H NMR Spectrum of Styrene Epoxide (100 MHz as a 5% solution in CCl_4)	61
Figure 5.12	The 60 MHz ^1H NMR Spectrum of a 4-Spin AMX_2 Spin System	62
Figure 5.13	Selective Decoupling in the ^1H NMR Spectrum of Bromoethane	64
Figure 5.14	Selective Decoupling in a Simple 4-Spin System	65
Figure 5.15	Characteristic Aromatic Splitting Patterns in the ^1H NMR Spectra for some Tri-substituted Benzenes	68

List of Figures

Figure 5.16	Characteristic Aromatic Splitting Patterns in the ^1H NMR Spectra for some Di-substituted Benzenes (ignoring the small <i>para</i> couplings)	68
Figure 5.17	^1H NMR Spectrum of <i>p</i> -Nitrophenylacetylene (200 MHz as a 10% solution in CDCl_3)	69
Figure 5.18	Aromatic Region of the ^1H NMR Spectrum of 2,4-Dinitrotoluene. (i) Basic NMR Spectrum; (ii) NMR Spectrum with Irradiation of the $-\text{CH}_3$ Group at δ 2.7; (iii) Difference Spectrum: Spectrum (ii) minus Spectrum (i)	70
Figure 5.19	D_2O Exchange in the ^1H NMR Spectrum of 1-Propanol (300 MHz, CDCl_3 solution)	71
Figure 6.1	^{13}C NMR Spectra of Methyl Cyclopropyl Ketone (CDCl_3 solvent, 100 MHz). (a) with Broadband Decoupling of ^1H ; (b) DEPT Spectrum (c) with no Decoupling of ^1H	74
Figure 7.1	Acquisition of a 2D NMR spectrum: a series of individual FIDs are acquired; each individual FID is subjected to a Fourier transformation; a second Fourier transformation in the remaining time dimension gives the final 2D spectrum	83
Figure 7.2	Representations of 2D NMR spectra: (a) Stacked plot; (b) Contour plot	83
Figure 7.3	Representations of Phase-sensitive 2D NMR spectra: (a) Stacked plot; (b) Contour plot	84
Figure 7.4	^1H COSY Spectrum of 1-Iodobutane (CDCl_3 solvent, 298K, 400 MHz)	85
Figure 7.5	^1H TOCSY Spectrum of Butyl Ethyl Ether (CDCl_3 solvent, 298K, 400 MHz)	87
Figure 7.6	^1H NOESY Spectrum of β -Butyrolactone (CDCl_3 solvent, 298K, 600 MHz)	88
Figure 7.7	^1H - ^{13}C <i>me</i> -HSQC Spectrum of 1-Iodobutane (CDCl_3 solvent, 298K, ^1H 400 MHz, ^{13}C 100 MHz)	90
Figure 7.8	^1H - ^{13}C HMBC Spectrum of 1-Iodobutane (CDCl_3 solvent, 298K, ^1H 400 MHz, ^{13}C 100 MHz)	92
Figure 7.9	^1H - ^{13}C HMBC Spectrum of 2-Bromophenol (CDCl_3 solvent, 298K, ^1H 400 MHz, ^{13}C 100 MHz)	94
Figure 8.1	Schematic NMR Spectra of Two Exchanging Nuclei	98
Figure 8.2	^1H NMR Spectrum of the Aliphatic Region of Cysteine	101

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.

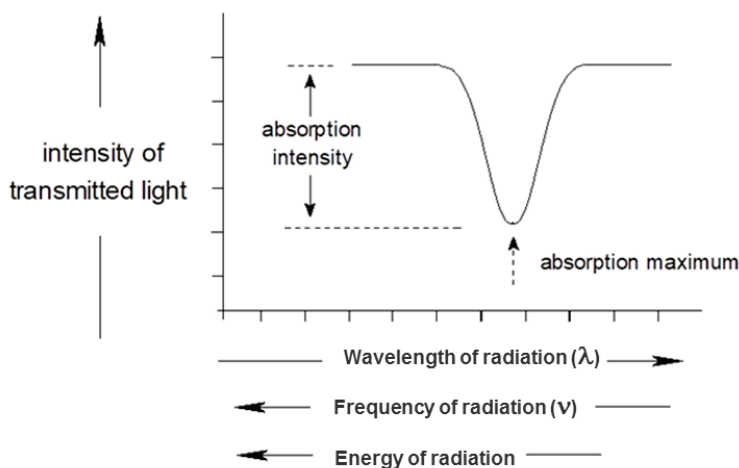


Figure 1.1 Schematic Absorption Spectrum

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:

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

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

Chapter 1 Introduction

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.

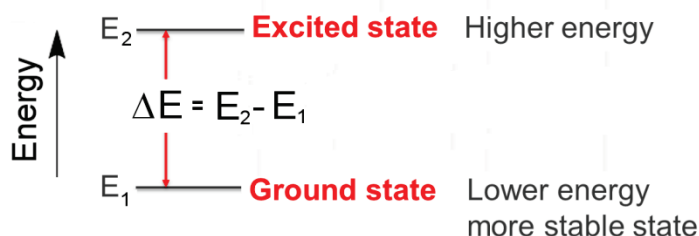


Figure 1.2 Definition of a Spectroscopic Transition

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

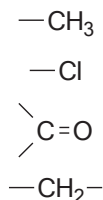
After these three steps, the molecular formula is reduced to C_nH_m and the degree of unsaturation is given by:

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

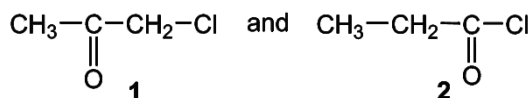
The degree of unsaturation indicates the number of π bonds or rings that the compound contains. For example, a compound whose molecular formula is $C_4H_9NO_2$ is reduced to C_4H_8 , which gives a degree of unsaturation of 1. This indicates that the molecule must have one π bond or one ring. Note that a triple bond (*e.g.* the $-C\equiv C-$ bond in an alkyne or the $-C\equiv N$ 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.* 1H 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:



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, ^1H 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 ^1H 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:

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

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.

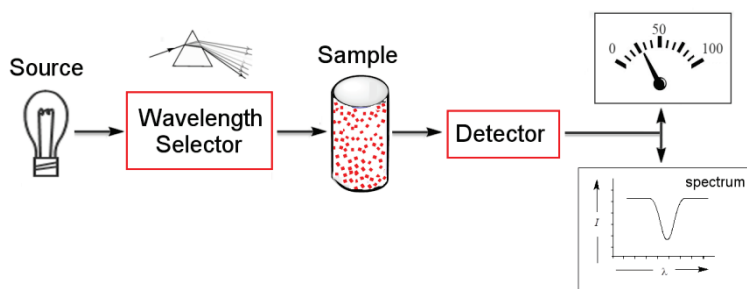


Figure 2.1 Schematic Representation of an IR or UV Spectrometer

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

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).

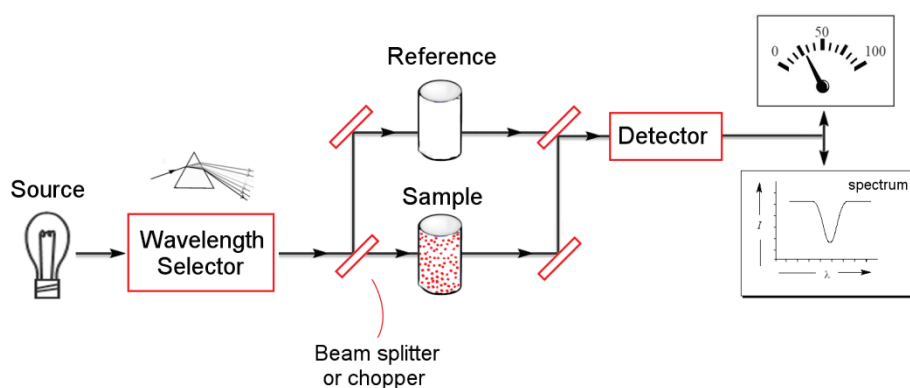


Figure 2.2 Schematic Representation of a Double-Beam Absorption Spectrometer

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).

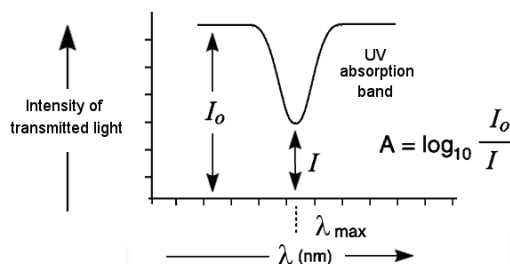


Figure 2.3 Definition of Absorbance (*A*)

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:

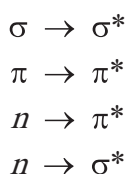
$$\epsilon = \frac{M A}{C l}$$

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 $\log_{10}(\epsilon)$ 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.*



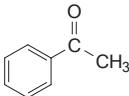
where *n* denotes a non-bonding orbital, the asterisk denotes an antibonding orbital and σ and π have the usual meaning in terms of bonding categories.

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

	$\lambda_{\max}(\text{nm})$	ϵ	$\log_{10}(\epsilon)$	Assignment	
 acetophenone	244	12,600	4.1	$\pi \rightarrow \pi^*$	K
	280	1,600	3.2	$\pi \rightarrow \pi^*$	B
	60	317	1.8	$n \rightarrow \pi^*$	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, –NR₂, –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 ($\epsilon > 200$) 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).

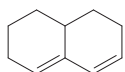
Table 2.2 The Effect of Extended Conjugation on UV Absorption

Alkene	λ_{\max} (nm)	ϵ	$\log_{10}(\epsilon)$
$\text{CH}_2=\text{CH}_2$	165	10,000	4.0
$\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_3$ (<i>trans</i>)	184	10,000	4.0
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	217	20,000	4.3
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$ (<i>trans</i>)	224	23,000	4.4
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$ (<i>trans</i>)	263	53,000	4.7
$\text{CH}_3-(\text{CH}=\text{CH})_5-\text{CH}_3$ (<i>trans</i>)	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:



$$\lambda_{\max} = 214 \text{ nm}$$

$$\epsilon = 16,000$$

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



$$\lambda_{\max} = 253 \text{ nm}$$

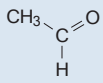
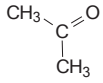
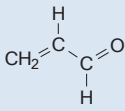
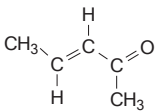
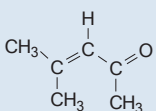

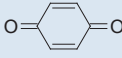
$$\epsilon = 8,000$$

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

2.6.2 CARBONYL COMPOUNDS

All carbonyl derivatives exhibit weak ($\epsilon < 100$) 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).


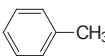

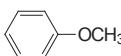
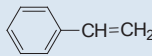
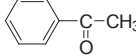
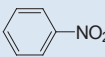
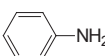
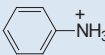
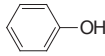

Table 2.3 UV Absorption Bands in Common Carbonyl Compounds

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

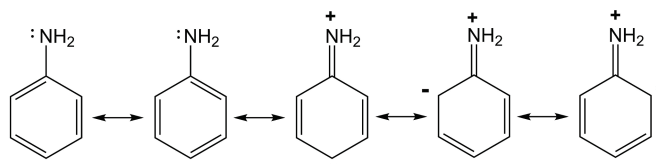
2.6.3 BENZENE DERIVATIVES

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 ($-\text{CH}_3$, $-\text{Cl}$, $-\text{OCH}_3$), groups which increase conjugation ($-\text{CH}=\text{CH}_2$, $-\text{C}(=\text{O})-\text{R}$, $-\text{NO}_2$) and auxochromes whose absorption is pH dependent ($-\text{NH}_2$ and $-\text{OH}$).

Table 2.4 UV Absorption Bands in Common Benzene Derivatives

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