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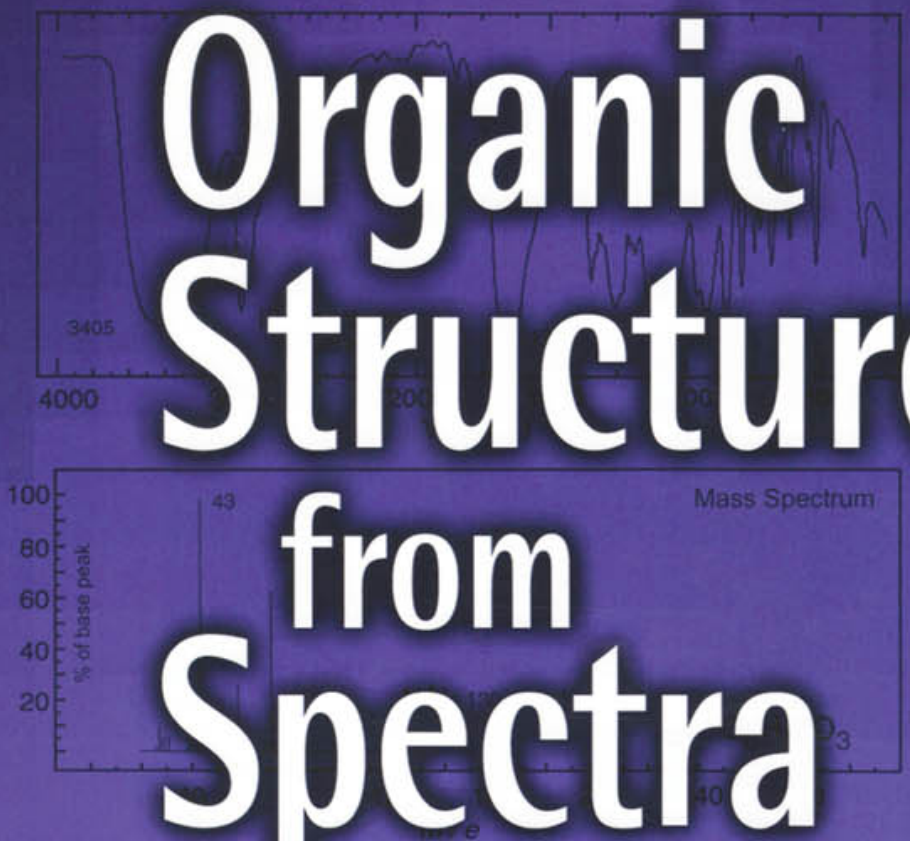
Organic Structures from Spectra



FIFTH EDITION

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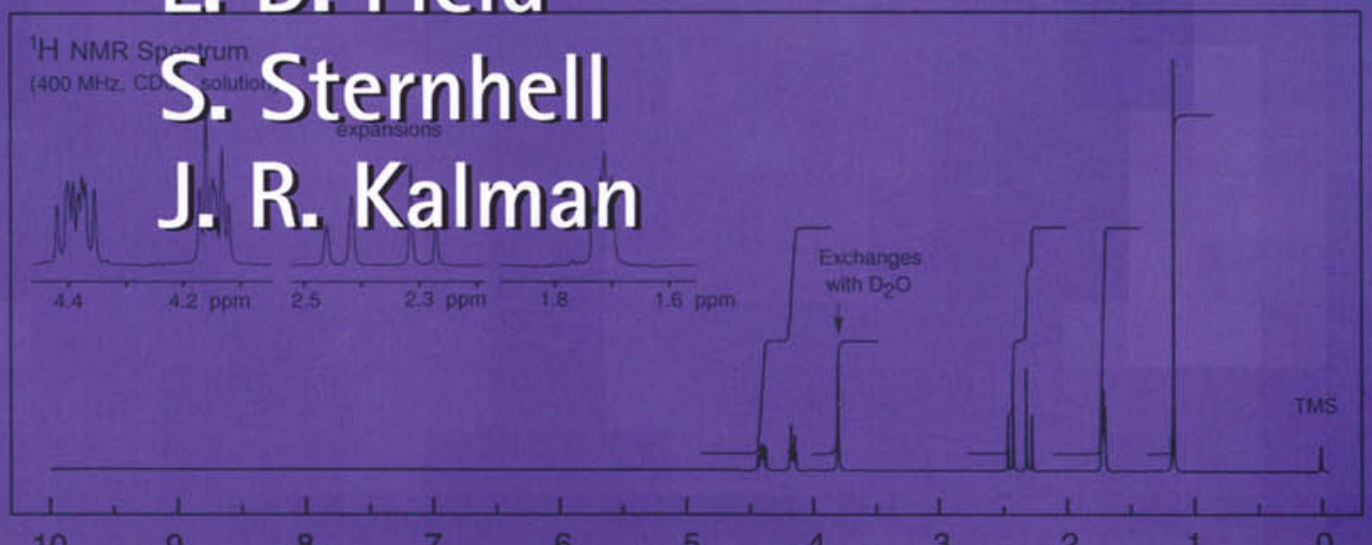

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Fifth Edition

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PREFACE

The derivation of structural information from spectroscopic data is an integral part of Organic Chemistry courses at all Universities. At the undergraduate level, the principal aim of courses in organic spectroscopy is to teach students to solve simple structural problems efficiently by using combinations of the major techniques (UV, IR, NMR and MS). Over a period more than 30 years, we have evolved courses at the University of Sydney and at the University of New South Wales, which achieve this aim quickly and painlessly. The text is tailored specifically to the needs and philosophy of these courses. As we believe our approach to be successful, we hope that it may be of use in other institutions.

The courses has been taught at the beginning of the third year, at which stage students have completed an elementary course of Organic Chemistry in first year and a mechanistically-oriented intermediate course in second year. Students have also been exposed, in their Physical Chemistry courses, 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 text of this book broadly corresponds to the material presented in the 9 lectures. The treatment is both elementary and condensed and, not surprisingly, the students have great difficulties in solving even the simplest problems at this stage. The lectures are followed by a series of 2-hour problem solving seminars with 5 to 6 problems being presented per seminar. 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, the real teaching is done during the hands-on problem seminars, which are organised in a manner modelled on that which we first encountered at the E.T.H. Zurich.

The class (typically 60 - 100 students, attendance is compulsory) is seated in a large lecture theatre in alternate rows and the problems for the day are identified. The students are permitted to work either individually or in groups and may use any written or printed aids they desire. Students solve the problems on their individual copies of this book thereby transforming it into a set of worked examples and most students voluntarily complete many more problems than are set. Staff (generally 4 or 5) wander around giving help and tuition as needed - the empty alternate rows of

seats make it possible to speak to each student individually. When an important general point needs to be made, the staff member in charge gives a very brief exposition at the board. There is a 1 ½ hour examination consisting essentially of 4 problems from the book and the results are in general very satisfactory. Moreover, the students themselves find 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.

Our philosophy can be summarised as follows:

(a) Theoretical exposition must be kept to a minimum, consistent with gaining of an understanding of the parts of the technique actually used in solving the problems. Our experience indicates that both mathematical detail and description of advanced techniques merely confuse the average student.

(b) The learning of data must be kept to a minimum. We believe that it is more important to learn to use a restricted range of data well rather than to achieve a nodding acquaintance with more extensive sets of data.

(c) Emphasis is placed on the concept of identifying "structural elements" and the logic needed to produce a structure out of the structural elements.

We have concluded that the best way to learn how to obtain "structures from spectra" is to practise on simple problems. This book was produced principally to assemble a suitable collection of problems for that purpose.

Problems 1-282 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 3 and 4; 19 and 20; 31 and 32; 42 and 43; 44, 45 and 46; 47, 48 and 49; 50 and 51; 61, 62 and 63; 64, 65 and 66; 81 and 82; 84 and 85; 99, 100, 101 and 102; 107 and 108; 110, 111, 112 and 113; 114 and 115; 118, 119 and 120; 122 and 123; 127 and 128; 139, 140, 141, 142 and 143; 155, 156, 157, 158, 159 and 160; 179 and 180; 181 and 182; 185 and 186; 215 and 216; 226 and 227; 235, 236 and 237; 276 and 277.

A further group of problems offer practice in the analysis of proton NMR spectra: 19, 20, 29, 37, 58, 75, 79, 90, 92, 93, 94, 99, 101, 123, 137, 146, 159, 163, 164, 183, 187, 192, 195, 205, 208, 236, 237, 238, 239, 248, 250, 251, 252 and 260.

A number of problems (195, 196, 197, 198, 230, 231, 260, 264, 265, 268, 271, 274 and 275) exemplify complexities arising from the presence of chiral centres, or from restricted rotation about peptide bonds (128, 162 and 262), while some problems deal with structures of compounds of biological, environmental, or industrial significance (22, 23, 36, 86, 95, 127, 131, 132, 144, 153, 162, 164, 197, 204, 220, 259, 260, 261, 263, 264, 265, 267, 272, 273, 274 and 275).

Problems 283-288 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 289-296 deal with the use of NMR spectroscopy for quantitative analysis and for the analysis of mixtures of compounds.

Problems 297-323 represent a considerably expanded set of problems dealing with the interpretation of two-dimensional NMR spectra and are a series of graded exercises utilising COSY, NOESY, C-H Correlation, HMBC and TOCSY spectroscopy as aids to spectral analysis and as tools for identifying organic structures from spectra.

Problems 324-346 deal specifically with more detailed analysis of NMR spectra, which tends to be a stumbling block for many students.

In Chapter 9, there are also two worked solutions (to problems 96 and 127) 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 or FAX: (61-2)-9385-8008

We wish to thank Dr Alison Magill, and Dr Hsiu Lin Li in the School of Chemistry at the University of New South Wales and Dr Ian Luck at the University of Sydney who helped to assemble the many additional samples and spectra in the 4th and 5th editions of this book. Thanks are also due to 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

S. Sternhell

J. R. Kalman September 2012

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1

INTRODUCTION

1.1 GENERAL PRINCIPLES OF ABSORPTION SPECTROSCOPY

The basic principles of absorption spectroscopy are summarised below. These are most obviously applicable to UV and IR spectroscopy and are simply extended to cover NMR spectroscopy. Mass Spectrometry is somewhat different and is not a type of absorption spectroscopy.

Spectroscopy is the study of the quantised interaction of energy (typically electromagnetic energy) with matter. In Organic Chemistry, we typically deal with molecular spectroscopy *i.e.* the spectroscopy of atoms that are bound together in molecules.

A schematic absorption spectrum is given in Figure 1.1. The absorption spectrum is a plot of absorption of energy (radiation) against its wavelength (λ) or frequency (ν).

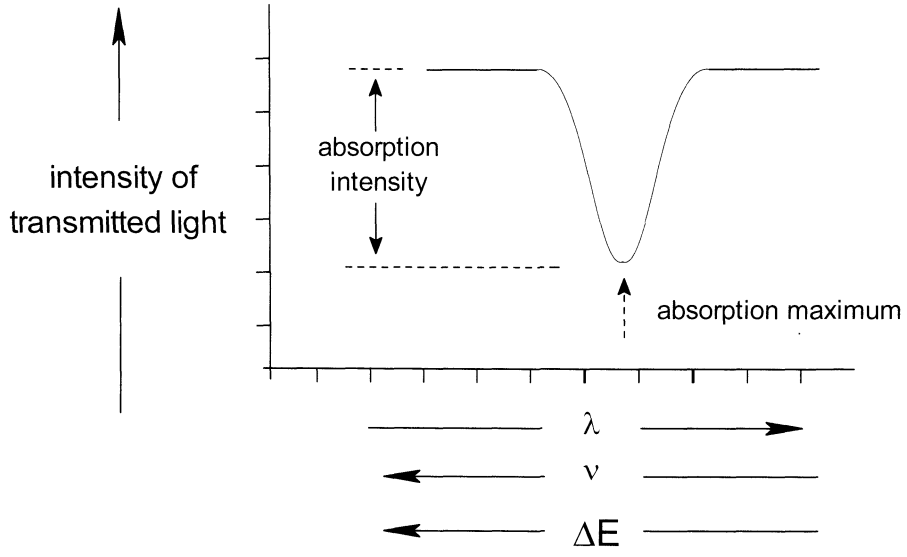


Figure 1.1 Schematic Absorption Spectrum

Organic Structures from Spectra, Fifth Edition. L. D. Field, S. Sternhell and J. R. Kalman.

An absorption band can be characterised primarily by two parameters:

(a) the wavelength 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 state to a state of a 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 the Planck's constant and ν is the frequency of the electromagnetic energy absorbed. Therefore $\nu \propto \Delta E$.

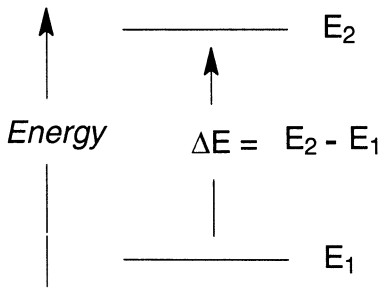


Figure 1.2 Definition of a Spectroscopic Transition

It follows that the x-axis in Figure 1.1 is an **energy** scale, since the frequency, wavelength and energy of electromagnetic radiation are interrelated:

$$\nu\lambda = c \text{ (speed of light)}$$

$$\lambda = \frac{c}{\nu}$$

$$\lambda \propto \frac{1}{\Delta E}$$

A spectrum consists of distinct bands or transitions because the absorption (or emission) of energy is quantised. The energy gap of a transition is a ***molecular property*** and is ***characteristic of molecular structure***.

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. 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) which 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 molecules as a whole that give rise to spectral features is fortunate, otherwise spectroscopy would only permit us to identify known compounds by direct comparison of their spectra with authentic samples. This "fingerprint" technique is often useful for establishing the identity of known compounds, but the direct determination of molecular structure building up from the molecular fragments is far more powerful.

1.3 DEGREE OF UNSATURATION

Traditionally, the molecular formula of a compound was derived from elemental analysis and its molecular weight which was 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 3 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

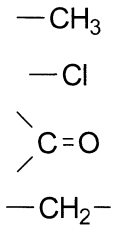
After these 3 steps, the molecular formula is reduced to C_nH_m and the degree of unsaturation is given by:

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

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 and this indicates that the molecule must have one π bond or one ring. Note 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. Conversely, if a compound has a degree of unsaturation greater than 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:

1 **2**

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) detect all chromophores accessible to them with equal sensitivity while in other techniques (*e.g.* UV) the range of sensitivity towards different chromophores spans many orders of magnitude. In terms of overall sensitivity, *i.e.* the amount of sample required, it is generally observed that:

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

but considerations of relative sensitivity toward different chromophores may be more important.

1.6 PRACTICAL CONSIDERATIONS

The 5 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 goes 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. 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 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 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 BASIC INSTRUMENTATION

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

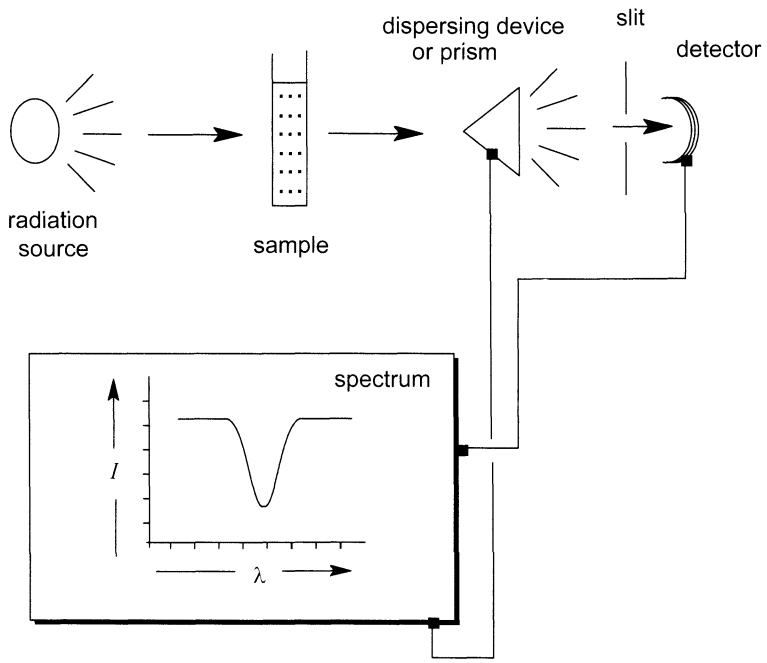


Figure 2.1 Schematic Representation of an IR or UV Spectrometer

The drive of the dispersing device is synchronised with the x-axis of the recorder or fed directly to a computer, so that this indicates 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 indicates how much radiation is absorbed by the sample at any particular wavelength.

Organic Structures from Spectra, Fifth Edition. L. D. Field, S. Sternhell and J. R. Kalman.

In practice, *double-beam* instruments are used where the absorption of a *reference cell*, containing only solvent, is subtracted from the absorption of the sample cell. Double beam instruments also cancel out absorption due to the atmosphere in the optical path as well as the solvent.

The energy source must be appropriate for the wavelengths of radiation being scanned. The materials from which the dispersing device and the detector are constructed must be as transparent as possible to wavelengths being scanned. For UV measurements, the cells and optical components are typically made of quartz and ethanol, hexane, water or dioxane are usually chosen as solvents.

2.2 THE NATURE OF ULTRAVIOLET SPECTROSCOPY

The term "UV spectroscopy" generally refers to *electronic transitions* occurring in the region of the electromagnetic spectrum (λ in the range 200-380 nm) accessible to standard UV spectrometers.

Electronic transitions are also responsible for absorption in the visible region (approximately 380-800 nm) which is easily accessible instrumentally but of less importance in the solution of 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.

2.3 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.* percentage of transmission or absorption), as is shown in Figure 2.2, or it may be calibrated on a logarithmic scale *i.e.* in terms of *absorbance* (A) defined in Figure 2.2.

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.

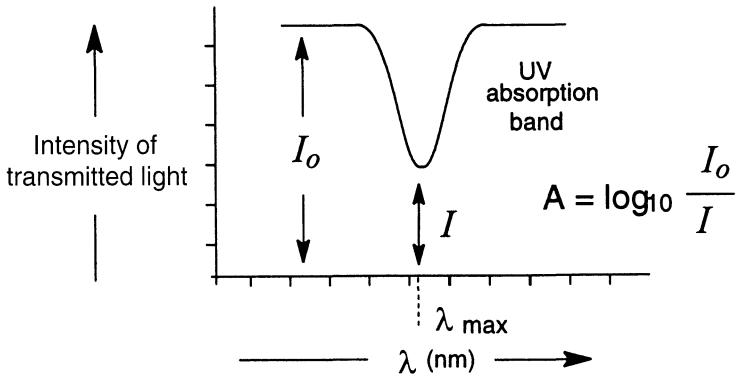


Figure 2.2 Definition of Absorbance (A)

UV absorption bands (Figure 2.2) 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 which are easier to manage. 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 due to 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.*

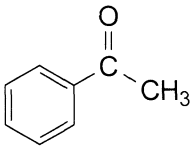
$$\sigma \rightarrow \sigma^*$$
$$\pi \rightarrow \pi^*$$
$$n \rightarrow \pi^*$$
$$n \rightarrow \sigma^*$$

where *n* denotes a non-bonding orbital, the asterisk denotes an antibonding orbital and σ and π have the usual significance.

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 3 easily observed bands:



acetophenone

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

2.5 SPECIAL TERMS IN UV SPECTROSCOPY

Auxochromes (auxiliary chromophores) are groups which 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 are 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 is due to relatively strongly absorbing chromophores ($\varepsilon > 200$) which are mainly indicative of conjugated or aromatic systems. Examples listed below encompass most of the commonly encountered effects.

(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 intensity (Table 2.1).

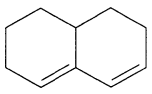
Table 2.1 The Effect of Extended Conjugation on UV Absorption

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 8 conjugated double bonds, the absorption maximum of polyenes is such that they absorb light strongly in the visible region of the spectrum.

Empirical rules (Woodward's Rules) of good predictive value are available to estimate 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

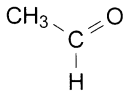
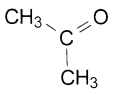
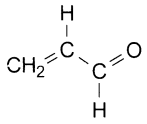
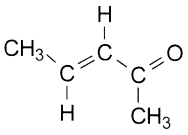
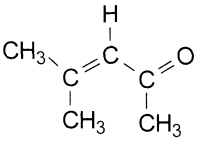
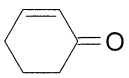
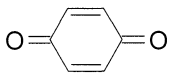
ε = 8,000

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

(2) 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 absorption (Table 2.2).

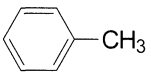
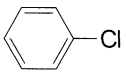
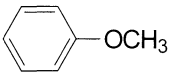
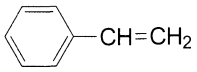
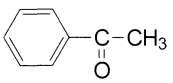
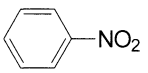
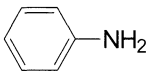
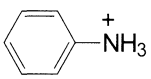
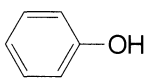
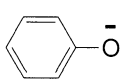
Table 2.2 UV Absorption Bands in Common Carbonyl Compounds

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

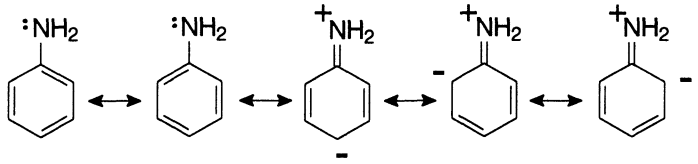
(3) Benzene derivatives

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 2.3 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 2.3 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 due to the overlap of the lone pair on the nitrogen (or oxygen) with the π-system of the benzene ring. This may be expressed in the usual Valence Bond terms:



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

2.7 THE EFFECT OF SOLVENTS

Solvent polarity may affect the absorption characteristics, in particular λ_{max}, since the polarity of a molecule usually changes when an electron is moved from one orbital to another. Solvent effects of up to 20 nm may be observed with carbonyl compounds. Thus the $n \rightarrow \pi^*$ absorption of acetone occurs at 279 nm in *n*-hexane, 270 nm in ethanol, and at 265 nm in water.

3

INFRARED (IR) SPECTROSCOPY

3.1 ABSORPTION RANGE AND THE NATURE OF IR ABSORPTION

Infrared absorption spectra are calibrated in wavelengths expressed in micrometers:

$$1\,\mu m = 10^{-6}\ m$$

or in frequency-related *wave numbers* (cm^{-1}) which are reciprocals of wavelengths:

$$\text{wave number } \bar{\nu}\ (cm^{-1}) = \frac{1 \times 10^4}{\text{wavelength (in } \mu m)}$$

The range accessible for standard instrumentation is usually:

$$\bar{\nu} = 4000 \text{ to } 666\ cm^{-1}$$

$$\text{or } \lambda = 2.5 \text{ to } 15\ \mu m$$

Infrared absorption intensities are rarely described quantitatively, except for the general classifications of s (strong), m (medium) or w (weak).

The transitions responsible for IR bands are due to *molecular vibrations, i.e.* to periodic motions involving stretching or bending of bonds. Polar bonds are associated with strong IR absorption ***while symmetrical bonds may not absorb at all.***

Clearly the vibrational frequency, *i.e.* the position of the IR bands in the spectrum, depends on the nature of the bond. Shorter and stronger bonds have their stretching vibrations at the higher energy end (shorter wavelength) of the IR spectrum than the longer and weaker bonds. Similarly, bonds to lighter atoms (*e.g.* hydrogen), vibrate at higher energy than bonds to heavier atoms.

IR bands often have rotational sub-structure, but this is normally resolved only in spectra taken in the gas phase.

Organic Structures from Spectra, Fifth Edition. L. D. Field, S. Sternhell and J. R. Kalman.