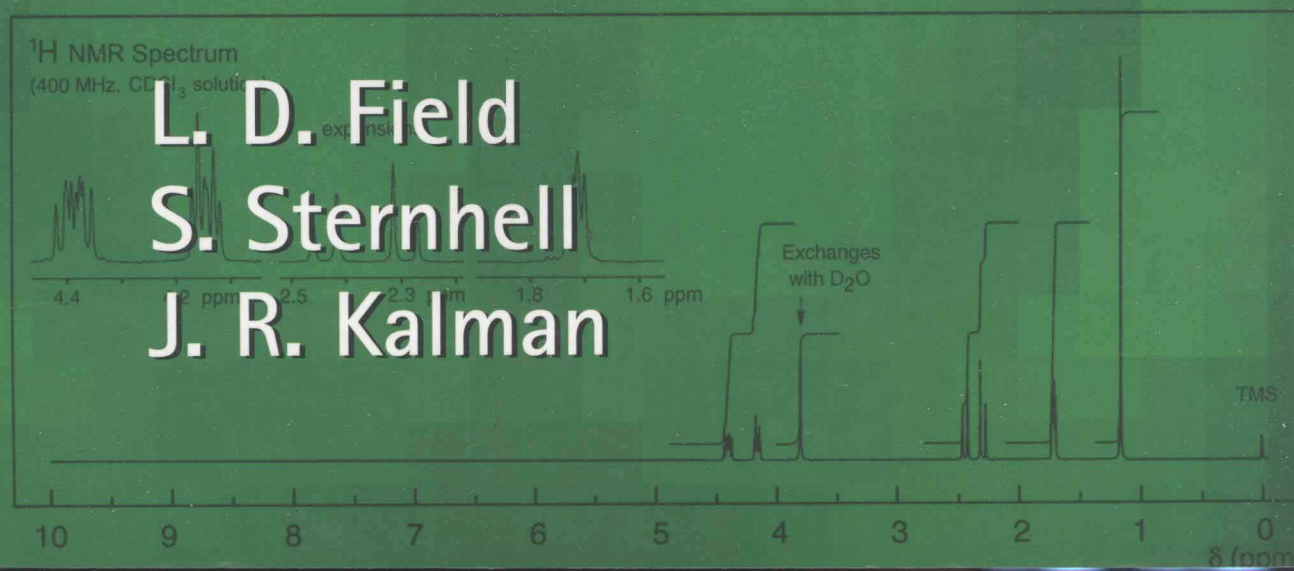
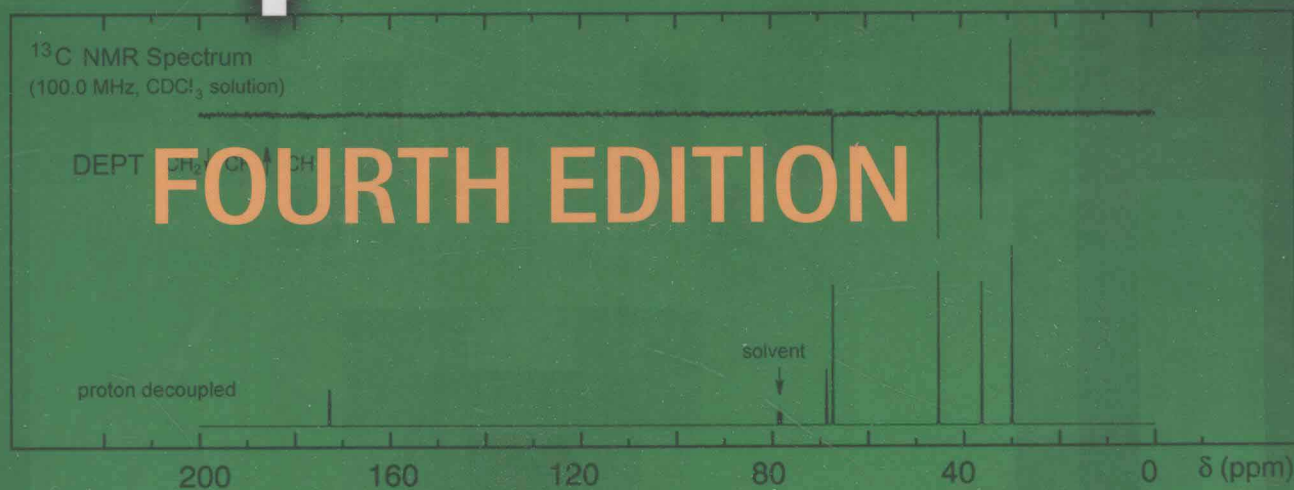
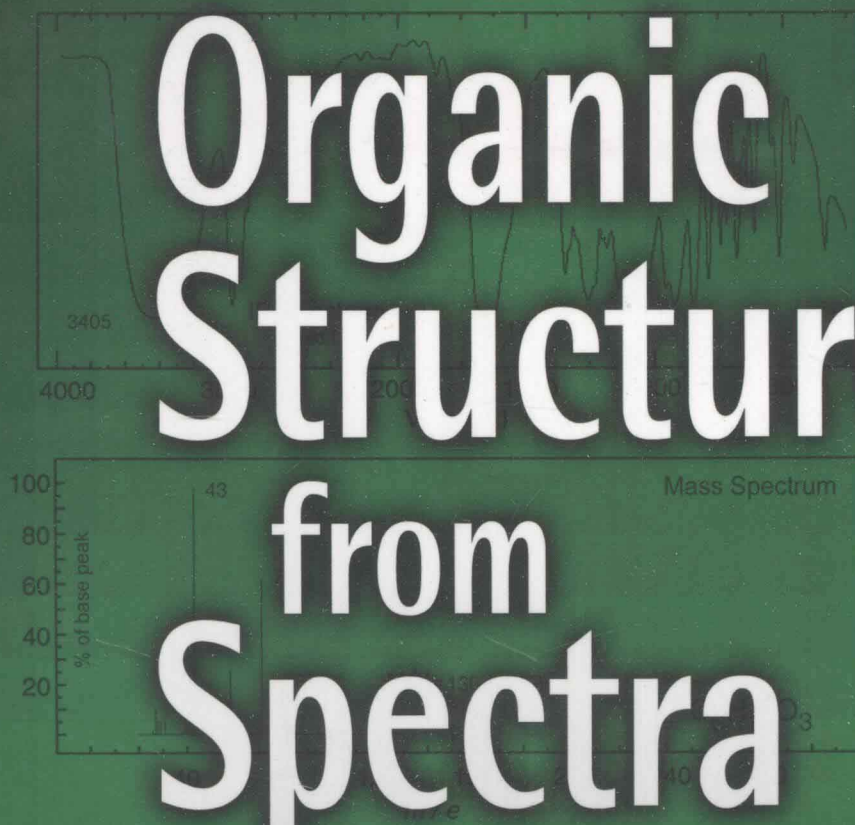


Organic Structures from Spectra



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Organic Structures from Spectra

Fourth Edition

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Organic Structures from Spectra

Fourth Edition

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 such courses is to teach students to solve simple structural problems efficiently by using combinations of the major techniques (UV, IR, NMR and MS), and over more than 25 years we have evolved a course at the University of Sydney, which achieves this aim quickly and painlessly. The text is tailored specifically to the needs and philosophy of this course. As we believe our approach to be successful, we hope that it may be of use in other institutions.

The course 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 it to the material presented in this course.

The course consists of about 9 lectures outlining the theory, instrumentation and the structure-spectra correlations of the major spectroscopic techniques and the text of this book 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 problem seminars, which are organised in a manner modelled on that used 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 we find that 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

Preface

making 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 1½ hour examination consisting essentially of 4 problems 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. There is also a real sense of achievement and understanding 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 collection of problems that we consider satisfactory for that purpose.

Problems 1 – 277 are of the standard "structures from spectra" type and are arranged roughly in order of increasing difficulty. A number of problems are groups of isomers which differ mainly in the connectivity of the structural elements and these problems are ideally set together (*e.g.* problems 2 and 3, 22 and 23; 27 and 28; 29, 30 and 31; 40 and 41; 42 to 47; 48 and 49; 58, 59 and 60; 61, 62 and 63; 70, 71 and 72; 77 and 78; 80 and 81; 94, 95 and 96; 101 and 102; 104 to 107; 108 and 109; 112, 113 and 114; 116 and 117; 121 and 122; 123 and 124; 127 and 128; 133 to 137; 150 and 151; 171 and 172; 173 and 174; 178 and 179; 225, 226 and 227; 271 and 272; and 275 and 276). A number of problems exemplify complexities arising from the presence of chiral centres (*e.g.* problems 189, 190, 191, 192, 193, 222, 223, 242, 253, 256, 257, 258, 259, 260, 262, 265, 268, 269 and 270); or of restricted rotation about peptide or amide bonds (*e.g.* problems 122, 153 and 255), while other problems deal with structures of compounds of biological, environmental or industrial significance (*e.g.* problems 20, 21, 90, 121, 125, 126, 138, 147, 148, 153, 155, 180, 191, 197, 213, 252, 254, 256, 257, 258, 259, 260, 266, 268, 269 and 270).

Problems 278 - 283 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 a report.

In the 4th Edition of "Organic Structures from Spectra" we have introduced problems dealing with quantitative analysis using NMR spectroscopy and problems 284 - 291 involve the analysis of mixtures of compounds.

In this edition, we have also introduced a series of problems using two-dimensional NMR. Problems 292 - 309 represent a graded series of exercises introducing COSY, NOESY, C-H Correlation and TOCSY spectroscopy as aids to spectral analysis and as tools for identifying organic structures from spectra.

Problems 310 - 332 deal with more detailed analysis of NMR spectra - this tends to be a stumbling block for many students. There are two worked solutions (to problems 91 and 121) in an Appendix 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 by writing to the authors or
EMAIL: L.Field@unsw.edu.au or FAX: (61-2)-9385-8008

We wish to thank Dr Ian Luck in the School of Chemistry at the University of Sydney, and Dr Hsiulin Li and Dr Adelle Shasha in the School of Chemistry at the University of New South Wales who helped to assemble the additional samples and spectra in the 4th edition 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 October 2007

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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).

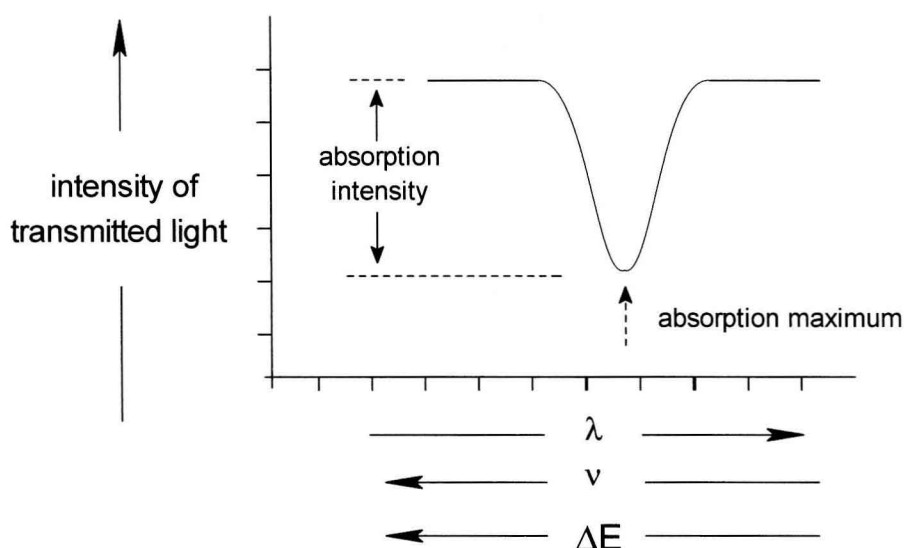


Figure 1.1 Schematic Absorption Spectrum

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 $\nu \propto \Delta E$.

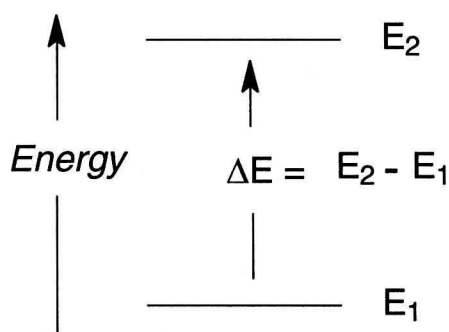


Figure 1.2 Definition of a Spectroscopic Transition

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

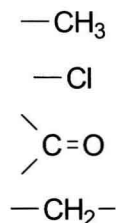
After these 3 steps, the molecular formula is reduced to C_nH_m and the degree of unsaturation is given by:

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

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:



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 ($-\text{CH}_3$) and methylene ($-\text{CH}_2-$) 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) 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, ^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 goes increasing difficulty in maintenance, 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 but the users require some training, computer skills and expertise. 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 by specialists.

- (c) The *scope* of each method can be defined as the amount of useful information it provides. This is a function not only of the total amount of information obtainable, but 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 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:

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