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Organic Structures from Spectra

FIFTH EDITION

L. D. Field
S. Sternhell
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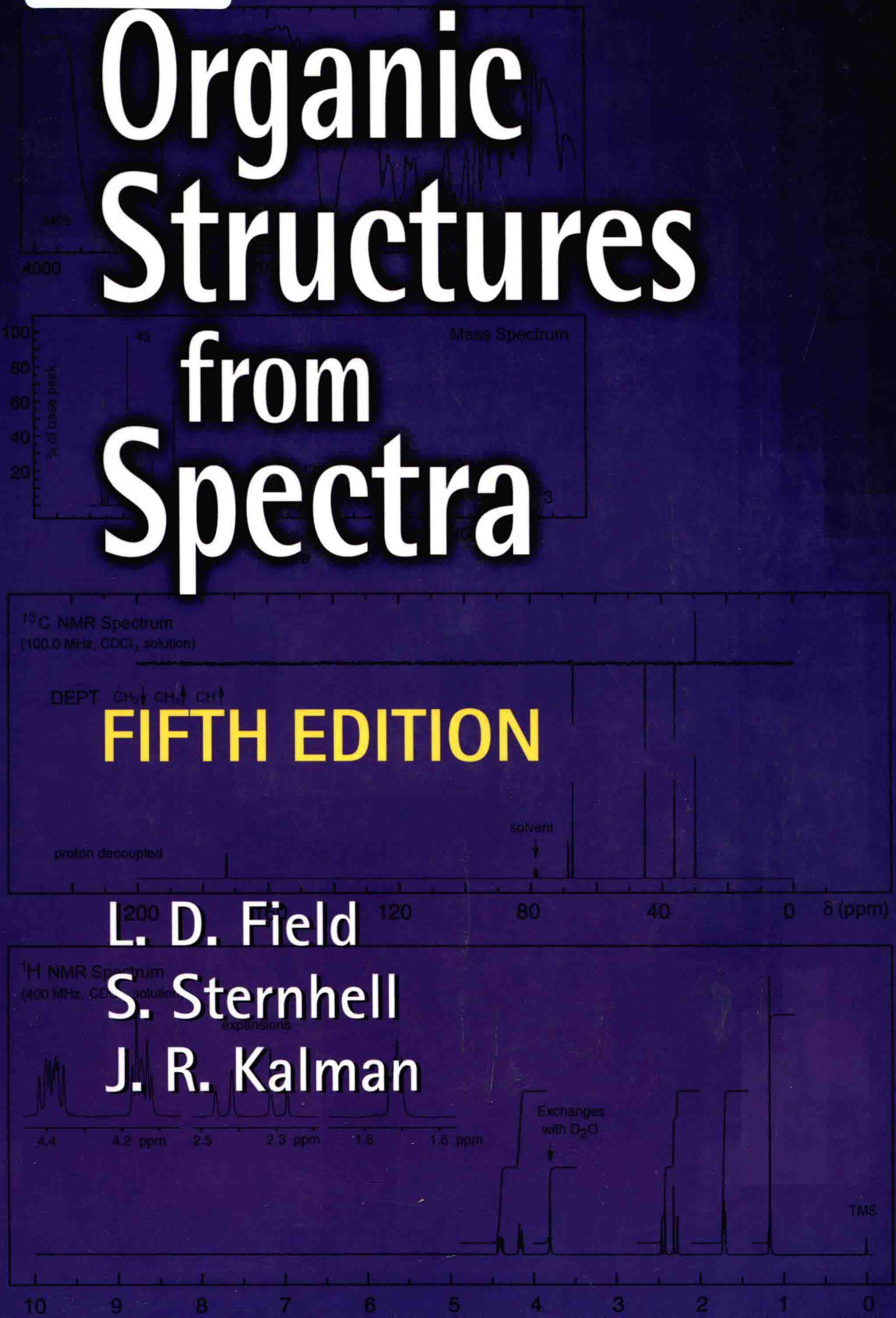

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PREFACE

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 1½ 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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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).

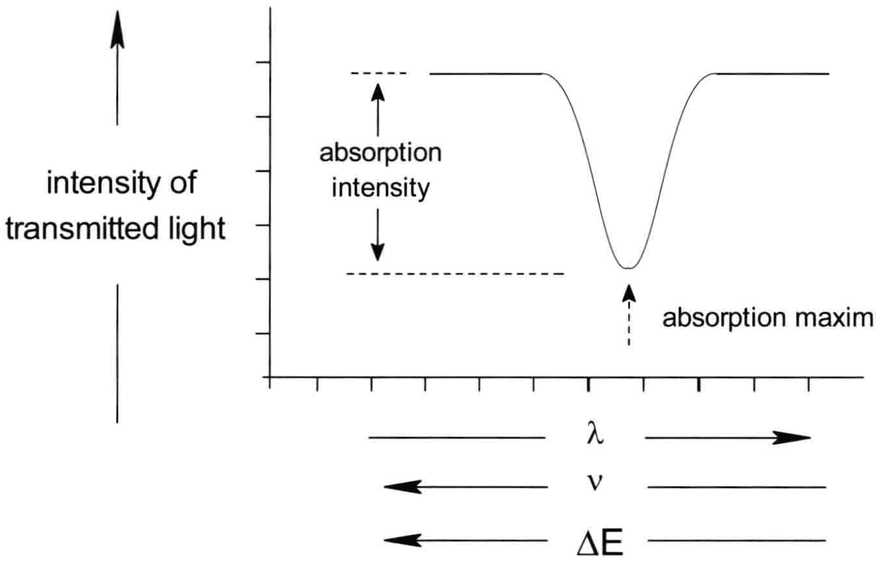

Figure 1.1 Schematic Absorption Spectrum

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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 $\nu \propto \Delta E$.

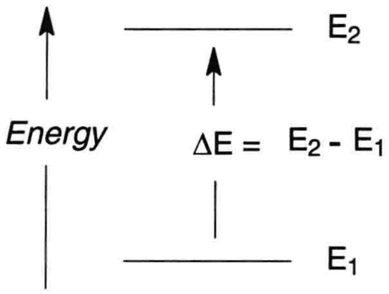

Figure 1.2 Definition of a Spectroscopic Transition

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:

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

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

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

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.