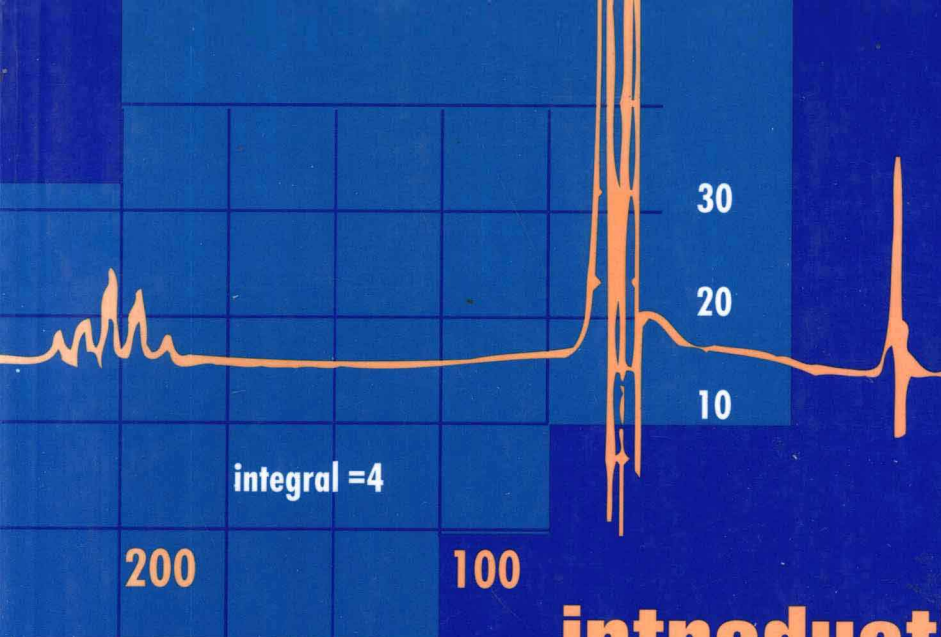
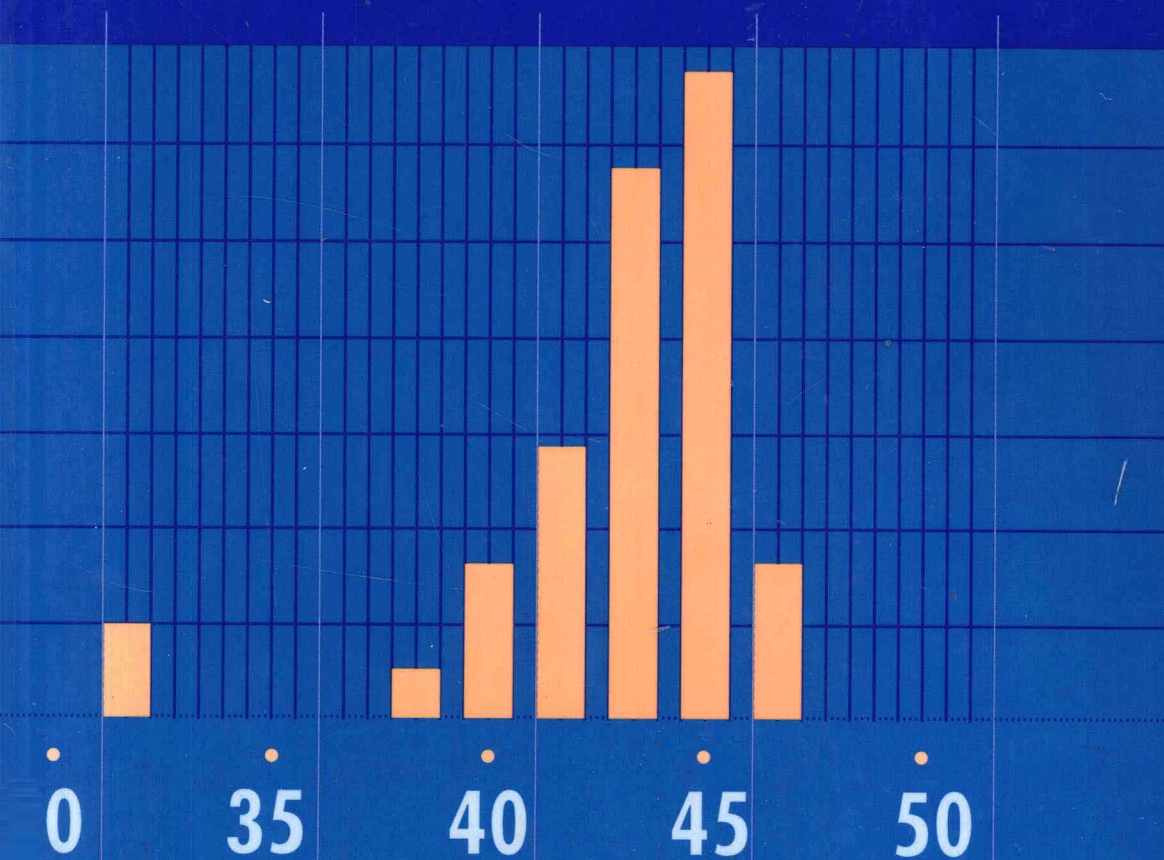


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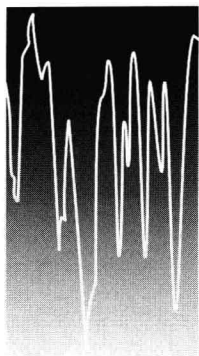
Pavia
Lampman
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introduction to



second
edition



INTRODUCTION TO SPECTROSCOPY

A GUIDE FOR STUDENTS OF ORGANIC CHEMISTRY

SECOND EDITION

DONALD L. PAVIA

GARY M. LAMPMAN

GEORGE S. KRIZ

DEPARTMENT OF CHEMISTRY
WESTERN WASHINGTON UNIVERSITY
BELLINGHAM, WASHINGTON



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TO OUR WIVES, NEVA-JEAN, MARIAN, AND CAROLYN

PREFACE

This book is an introductory text in spectroscopy for students of organic chemistry. It can serve as a supplement for the typical organic chemistry lecture textbook and can also be used as a stand-alone textbook for an undergraduate course in spectroscopic methods of structure determination or as a tool for students engaged in research. Our intent is to create a book of an intermediate level of difficulty, one that undergraduate students can understand, even if they lack an extensive background in physics or mathematics. We have tried not to dwell excessively on difficult aspects of theory but have nonetheless attempted to cover the important aspects of each spectroscopic technique. Our goal is to teach students to interpret spectra.

This text has evolved over the years from materials we have used in our own classes at a predominantly undergraduate institution. We have sometimes used these materials as a supplement in our one-year sequence of organic chemistry, but more frequently we have used the book as a textbook in a hands-on, one-quarter, junior–senior-level course in spectroscopic methods of identifying organic compounds. Our students also learn to use an FT-IR, a 300-MHz FT-NMR, diode-array spectrophotometers, a GC/MS, and a variety of computer software. (The use of instrumentation is optional because of the availability of many fine spectral libraries and some very useful computer software programs.) We have found our lecture approach to be very successful with our students, and we believe that this textbook should prove useful with courses taught in other institutions.

Each chapter of our text includes examples and a large number of problems to provide students sufficient practice to master the material presented. In addition, Chapter 8 consists of a number of *combined problems*, which use information gathered by the various spectroscopic methods (not always the same ones) to reach a structure determination. Our philosophy of using large numbers of drill problems to reinforce the discussions in the book is reflected in these problems. Answers to the problems are provided at the end of the book.

This second edition of INTRODUCTION TO SPECTROSCOPY contains a number of additions. Our previous edition, published 18 years ago (!) when some of the current techniques were not in common use, did not cover FT-NMR, 2D-NMR, or carbon-13 NMR; nor did it cover nuclei other than hydrogen. This new edition covers each of these techniques in detail. Among the new chapters is one on two-dimensional NMR techniques. Because some instructors may consider this to be advanced material and beyond the scope of their courses, we have placed this new chapter at the end of the book (Chapter 9). We have also tried to show clearly the differences between NMR spectra determined at high field and those obtained at low field. We have added a great many 300-MHz spectra, but, for pedagogic reasons, we have decided not to replace all of the 60-MHz low-field spectra. The book incorporates a mix of the two.

We would like to thank all of you who have stuck with us for the last 18 years, urging us all the while to update our book. Foremost among you we must thank John Vondeling, whose persistent nagging has finally yielded fruit. We certainly hope that this updated version will satisfy your expectations.

We wish to express our gratitude to the people who assisted us with the preparation of this manuscript. Armando Herbelin helped a great deal by writing automation programs for our Bruker AC-300 that gave good routine results and were usable by students. Thanks, Armando, for keeping our instrument going strong and with good resolution! Special thanks go to Brenda Crook Luciano, who determined many of the 2D-NMR spectra. Aaron Skiffington contributed his time to run spectra. We also offer our sincere thanks to Dr. Jerrold Grayson and to the Magnetic Resonance Imaging Laboratory of St. Joseph Hospital, Bellingham, Washington, for providing us examples of magnetic resonance images. Special thanks are due to the students in our spectroscopy classes for the stimulation they provide us.

We wish to acknowledge the cooperation of Varian Associates and the Aldrich Chemical Company for their permission to use infrared and nuclear magnetic resonance spectra from their catalogues.

Many of our colleagues reviewed the manuscript and provided helpful criticism: Professors Eric Anslyn (University of Texas at Austin), Ken Brown (St. Mary's College of California), Robert G. Carlson (University of Kansas), Seth Elsheimer (University of Central Florida), Gene D. Schaumberger (Sonoma State University), David A. Shultz (North Carolina State University), William F. Wood (Humboldt State University), and Chang Wu (University of Massachusetts at Dartmouth). Saunders College Publishing and York Graphic Services capably handled production of this textbook. We thank all who contributed, with special thanks to our project editors, Laura Shur and Sarah Fitz-Hugh. As always, we thank Sandi Kiselica, our developmental editor, who kept encouraging us to write and who worked hard to make this textbook possible.

Finally, we wish to thank our wives, Neva-Jean, Marian, and Carolyn, and our children for their patience and understanding. They will certainly be pleased to finally have us at home in the evenings.

Donald L. Pavia
Gary M. Lampman
George S. Kriz

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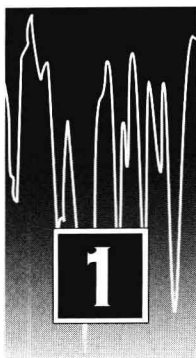
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MOLECULAR FORMULAS AND WHAT CAN BE LEARNED FROM THEM

Before attempting to deduce the structure of an unknown organic substance from an examination of its spectra, we can simplify the problem somewhat by examining the molecular formula of the substance. The purpose of this chapter is to describe how the molecular formula of a compound is determined and how structural information may be obtained from that formula. The early portion of this chapter reviews the classical analytical methods of determining a molecular formula. Many of these methods are still in routine use today, but the use of mass spectrometry has become a common alternative. A brief introduction to the use of the mass spectrometer is given at the end of this chapter (Section 1.6) and in Chapter 7.

1.1 ELEMENTAL ANALYSIS AND CALCULATIONS

The classical process of determining the molecular formula of a substance involves three steps. The first step is to perform a **qualitative elemental analysis** in order to find out what kinds of atoms are present in the molecule. The second step is to perform a **quantitative elemental analysis** in order to determine the relative numbers of the distinct kinds of atoms in the molecule. This analysis leads to an **empirical formula**. The third step is a **molecular mass determination** (or **molecular weight determination**) which, when combined with the empirical formula, shows the actual numbers of the distinct kinds of atoms. The result is the **molecular formula**.

Virtually all organic compounds contain carbon and hydrogen. In most cases it is not necessary to determine whether these elements are present; their presence is assumed. However, if it should be necessary to demonstrate that either carbon or hydrogen is present in a compound, that substance may be burned in the presence of oxygen. If combustion produces carbon dioxide, carbon must have been present in the unknown material; if combustion produces water, hydrogen atoms must have been present in the unknown.

It is important to note that there is no suitable direct method for determining the presence of oxygen in a substance. Consequently, the presence of oxygen is not demonstrated in a qualitative analysis.

Nitrogen, chlorine, bromine, iodine, and sulfur may be identified by tests similar to the **sodium fusion test**. To obtain the details of such tests, you should consult a textbook on qualitative organic analysis. The reference list at the end of this chapter includes examples of suitable textbooks.

To determine the precise amounts of carbon and hydrogen present in an unknown substance, a quantitative analysis is required. In practice, commercial laboratories frequently perform such analyses. The method of determining the amounts of carbon and hydrogen in a substance involves combustion to carbon dioxide and water. In a quantitative analysis, the carbon dioxide and water are collected and weighed. Methods are also available for the determination of the amounts of sulfur, nitrogen, and halogens which may be present. The mathematical methods for determining the percentage composition of an unknown substance from quantitative analysis for the elements should be familiar from general chemistry. For review, however, Table 1.1 summarizes the calculation of percentage composition, using an unknown organic compound as an example. Notice in the sample calculation that the percentage of oxygen in a sample is generally determined by difference.

It is quite rare to find a research laboratory in which elemental analyses are performed by classical methods. Usually samples are sent to a commercial analytical laboratory which specializes in quantitative elemental analyses, or modern instrumentation is used. The commercial laboratory returns a report which lists the percentages of carbon and hydrogen in the sample. The report also includes the percentages of any other elements requested. In either case, the principles outlined in this section still apply, but the procedures tend to be too time-consuming to be conducted in every organic chemistry laboratory.

Commercially available elemental analyzers are capable of determining simultaneously the percentages of carbon, hydrogen, and nitrogen in a compound. In these instruments, the sample is burned in a stream of oxygen. The gaseous products are converted to carbon dioxide, water, and nitrogen, which can be detected via gas chromatography, using thermal conductivity detectors. The precise amount of each gas produced in the combustion is determined by integration of the corresponding gas chromatography peaks. Some instruments are capable of performing oxygen analyses.

TABLE 1.1

Calculation of Percentage Composition from Combustion Data



$$9.83 \text{ mg} \qquad 23.26 \text{ mg} \quad 9.52 \text{ mg}$$

$$\text{millimoles CO}_2 = \frac{23.26 \text{ mg CO}_2}{44.01 \text{ mg/mmol}} = 0.5285 \text{ mmol CO}_2$$

$$\text{mmol CO}_2 = \text{mmol C in original sample}$$

$$(0.5285 \text{ mmol C})(12.01 \text{ mg/mmol C}) = 6.35 \text{ mg C in original sample}$$

$$\text{millimoles H}_2\text{O} = \frac{9.52 \text{ mg H}_2\text{O}}{18.02 \text{ mg/mmol}} = 0.528 \text{ mmol H}_2\text{O}$$

$$(0.528 \text{ mmol H}_2\text{O}) \left(\frac{2 \text{ mmol H}}{1 \text{ mmol H}_2\text{O}} \right) = 1.056 \text{ mmol H in original sample}$$

$$(1.056 \text{ mmol H})(1.008 \text{ mg/mmol H}) = 1.06 \text{ mg H in original sample}$$

$$\% \text{ C} = \frac{6.35 \text{ mg C}}{9.83 \text{ mg sample}} \times 100 = 64.6\%$$

$$\% \text{ H} = \frac{1.06 \text{ mg H}}{9.83 \text{ mg sample}} \times 100 = 10.8\%$$

$$\% \text{ O} = 100 - (64.6 + 10.8) = 24.6\%$$

TABLE 1.2

Calculation of Empirical Formula

Using a 100-g sample:

$$64.6\% \text{ of C} = 64.6 \text{ g}$$

$$10.8\% \text{ of H} = 10.8 \text{ g}$$

$$24.6\% \text{ of O} = \frac{24.6 \text{ g}}{100.0 \text{ g}}$$

$$\text{moles C} = \frac{64.6 \text{ g}}{12.01 \text{ g/mole}} = 5.38 \text{ moles C}$$

$$\text{moles H} = \frac{10.8 \text{ g}}{1.008 \text{ g/mole}} = 10.7 \text{ moles H}$$

$$\text{moles O} = \frac{24.6 \text{ g}}{16.0 \text{ g/mole}} = 1.54 \text{ moles O}$$

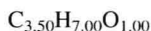
giving the result



Converting to the simplest ratio:

$$\frac{\text{C}_{5.38}\text{H}_{10.7}\text{O}_{1.54}}{\frac{1.54}{1.54} \frac{10.7}{1.54} \frac{5.38}{1.54}} = \text{C}_{3.49}\text{H}_{6.95}\text{O}_{1.00}$$

which approximates



or



The percentage composition result may be used to calculate the empirical formula of the substance being studied. Note that the empirical formula expresses the correct **simplest whole-number ratios** of the elements in the test substance. The empirical formula may not be the true, or molecular, formula of the substance being examined. The molecular formula may be some multiple of the empirical formula. The mathematical methods used to obtain the empirical formula are familiar from general chemistry. As an illustration, however, a sample calculation, using the same unknown sample that was presented earlier, is shown in Table 1.2.

1.2 DETERMINATION OF MOLECULAR MASS

The next step in determining the molecular formula of a substance is to determine the weight of one mole of that substance. This may be accomplished in a variety of ways. Without knowledge of the molecular mass of the unknown, there is no way of telling whether the empirical formula, which is determined directly from elemental analysis, is the true formula of the substance or whether the empirical formula must be multiplied by some integral factor to obtain the molecular formula. In the example cited in Section 1.1, without knowledge of the molecular mass of the unknown, it is impossible to tell whether the molecular formula is $\text{C}_7\text{H}_{14}\text{O}_2$ or $\text{C}_{14}\text{H}_{28}\text{O}_4$.

In a modern laboratory, the molecular mass is determined through the use of mass spectrometry. The details of this method and the means of determining molecular mass can be found in Section 1.6 and Chapter 7, Section 7.4. This section reviews some classical methods of obtaining the same information.

An old method for determining the molecular mass of the substance, based on general chemistry principles, is the **vapor density method**. In this method, a known volume of gas is weighed at a known temperature. After converting the volume of the gas to standard temperature and pressure, we can determine what fraction of a mole that volume represents. From that fraction, we can easily calculate the molecular mass of the substance.

Another method of determining the molecular mass of a substance is to measure the freezing-point depression of a solvent that is brought about when a known quantity of test substance is added. This is known as a **cryoscopic method**. Another method, which is used occasionally, is **vapor pressure osmometry**, in which the molecular weight of a substance is determined through an examination of the change in vapor pressure of a solvent when a test substance is dissolved in it.

If the unknown substance is a carboxylic acid, it may be titrated with a standardized solution of sodium hydroxide. By use of this procedure, a **neutralization equivalent** can be determined. The neutralization equivalent is identical to the equivalent weight of the acid. If the acid has only one carboxyl group, the neutralization equivalent and the molecular mass are identical. If the acid has more than one carboxyl group, the neutralization equivalent is equal to the molecular mass of the acid divided by the number of carboxyl groups. Many phenols, especially those substituted by electron-withdrawing groups, are sufficiently acidic to be titrated by this same method, as are sulfonic acids.

1.3 MOLECULAR FORMULAS

Once the molecular mass and the empirical formula are known, one may proceed directly to the **molecular formula**. Often the empirical formula weight and the molecular mass are the same. In such cases, the empirical formula is also the molecular formula. However, in many cases, the empirical formula weight is less than the molecular mass, and it is necessary to determine how many times the empirical formula weight can be divided into the molecular mass. The factor determined in this manner is the one by which the empirical formula must be multiplied in order to obtain the molecular formula.

Ethane provides a simple example. After quantitative element analysis, the empirical formula for ethane is found to be **CH₃**. A molecular mass of 30 is determined. The empirical formula weight of ethane, 15, is half of the molecular mass, 30, two times. Therefore, the molecular formula of ethane must be 2(CH₃) or C₂H₆.

For the sample unknown introduced earlier in this chapter, the empirical formula was found to be C₇H₁₄O₂. The formula weight is 130. If we assume that the molecular mass of this substance was determined to be 130, we may conclude that the empirical formula and the molecular formula are identical and that the molecular formula must be C₇H₁₄O₂.

1.4 INDEX OF HYDROGEN DEFICIENCY

Frequently, a great deal can be learned about an unknown substance simply from a knowledge of its molecular formula. This information is based on the following general molecular formulas.