Principles of Ultraviolet Photoelectron Spectroscopy

J. Wayne Rabalais, University of Houston. John Wiley & Sons, New York, 1977. xx + 454 pages. Figs. and tables. 16 x 23.5 cm. $29.95.

"Principles of Ultraviolet Photoelectron Spectroscopy" by J. W. Rabalais is a welcome addition to the literature of ultraviolet photoelectron spectroscopy. The text extends the earlier, more qualitative treatments by Turner, Eland, and Baker to provide a more rigorous and detailed description of photoemission and photoelectron spectra. Although this edition loses some of the pictorial clarity of the other monographs, it does reflect the present trend toward a more quantitative understanding of photoelectron spectra through comparison with results from molecular orbital calculations.

After a brief introductory and experimental sections, the author opens the main portion of the book with a discussion of the process of photoionization and a survey of the molecular factors which affect the number, energy, and distribution of the photoelectrons emitted. The material surveyed very briefly here is expanded and more adequately discussed in the following chapters. The first of these more detailed and better written chapters starts with a discussion concerning the use of results from molecular orbital calculations as mathematical models for matching and predicting the energies and, in the next chapter, the relative numbers of photoelectrons produced. These discussions include a rationale for the continued use of Koopmans theorem in photoelectron spectroscopy. Next the finer effects from spin-orbit coupling and molecular distortions (Jahn-Teller and Renner) are considered and illustrated with some nicely worked examples. Finally the author treats the simplifications used to interpret the more complex spectra of larger molecules (e.g., benzene and ferrocene) and then mentions some interesting applications of photoelectron spectroscopy. Also listed in the last chapter is a summary of the key points used in interpreting spectra and deducing the origin(s) of the spectral bands. Filling out the remainder of the text are a series of appendices of supplementary material including an index of references to photoelectron spectra listed by molecular size and chemical composition. The references cited are mainly drawn from 1973 to early 1975 but do reach back to 1966.

The strongest points of the book are the authors inclusion of the most recent theories and developments possible as illustrated by the dates of the references, the collected listing of methods used to simplify the interpretation of photoelectron spectra, and the comprehensive treatment of the mathematical models used to confirm the interpretation. The book is not without weaker points. A firm grounding in molecular orbital theory is assumed and, to fully appreciate many of the discussions, an understanding of molecular spectroscopy and group theory is required. In several chapters, particularly chapter two, the discussions could be better organized and written to aid the reader. Finally the brevity of application sections leaves the reader without a true feeling of the contribution that photoelectron spectroscopy is making in chemistry, surface science, and chemical physics. Comparing these few criticisms to the positive contribution of the remainder of the book, this reviewer certainly can strongly recommend this monograph to advanced undergraduates, graduates students, and certainly research workers in the field of photoelectron spectroscopy, as well as to workers in the areas of experimental molecular spectroscopy and quantum mechanics.

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Organic Structural Analysis

Joseph B. Lambert, Northwestern University, Herbert F. Shropshire, Queen's University, Lawrence Verbit, State University of New York at Binghamton, R. Graham Cooks, Purdue University, and George H. Stout, University of Washington. Macmillan Publishing Co., Inc., New York, 1976. xii + 596 pages. Figs. and tables. 15 7/8 x 26 cm. $22.95.

This book is designed to introduce the organic chemist to the major fields of spectroscopy. The authors' objectives are stated in the preface. "The five parts of this book are intended to have the flavor of both the elementary and the state-of-the-art, so that the practicing chemist can obtain authoritative treatments of all subjects under one cover, but the beginner can still expect a clear introduction. The subjects covered are nmr, ir, and Raman, Mass Spectroscopy and X-ray crystallography.

Each part of the book is written by one author. Experimental methods, theory, and applications are given. Generally, a bibliography is given by each author after each subdivision of his chapter. The "Vibrational Spectroscopy" chapter contains extensive correlation tables and an appendix, "Using the Literature on Vibrational Spectra." The "Mass Spectroscopy" chapter contains an appendix, "Worked Structural Problems."

The value of this book to the beginner lies in its tables, appendices, and references. The problems that are worked out are useful and helpful. However, the difficulties in this "one-cover" approach are illustrated by the X-ray chapter, in which the references indicate a much more extensive treatment is needed for comprehension.

Overall, I do not think the authors achieved their stated objective with this book.

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Classics in Coordination Chemistry
Part II: Selected Papers (1789—1899)


The story of Werner's discovery of the Coordination Theory is well known—his sudden awakening at two o'clock in the morning in a flash of genius, with the theory complete in his mind, and his rising to write it ready for publication that same day. It is often assumed from that account that Werner had no precedent, but that the theory came out of clear, thin air. Such, of course, is not the case—coordination compounds had been known for nearly a century, and there had been many attempts to explain their formation and structures. Most of these theories were concerned with the metal ammines, and were based on the theories of organic chemistry; chains of nitrogen atoms replacing the chains of carbon atoms. A few, however, were much closer to Werner's Coordination Theory. For example, in 1885 Horstmann wrote the formula of potassium hexachloroplatinate(IV) as

\[
\begin{align*}
\text{KCl}_2 & \cdot \text{PtCl}_4 \\
& \cdot \text{PtCl}_4 \cdot \text{KCl}_2
\end{align*}
\]

This differs from Werner's formulation only in that it does not differentiate between the Pt-Cl and the Pt-K bonds.

Werner certainly knew of these earlier theories, and he synthesized a new theory from them. Not that this detracts from his genius or his great contribution—far from it! He was the one who saw that there must be two types of valence bonds and he was able to include the ammines, the hydrates, and the double salts in a single theory. He was undoubtedly the great chemical genius of his time, and he deserves all of the credit that has been accorded him.

But, it is important, too, to recognize the men who preceded him and who, in fact, furnished the basis for his theory.

In this interesting and useful little book, Professor Kauffman has assembled translations of important papers by six of Werner's predecessors—Magnus, Zeise, Graham, Claus, Blomstrand, and Jørgensen. Each paper is preceded by an introduction which tells something of the life and work of the author of that paper; in addition, footnotes referring to other works often give historical and biographical bits that enliven the account. The translations in this book are freer than those in Part I, so are easier and more pleasant to read. For anyone who is interested in the history of chemistry, this volume is more fun than a whodunit. And more educational, too.

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