enhancements observed in this study are significant and promise to be applicable to a variety of problems. For example, in mobile systems[11] that do not cross polarize efficiently, single-pulse experiments with NOE enhancement could be a superior alternative. NOE measurements in solids may also be useful for probing high-frequency motions, for studying relaxation mechanisms and pathways, and for spectral assignments.

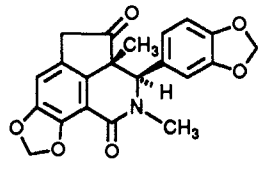
Acknowledgment. This work was supported by grants for the National Science Foundation (CHE-8918741) and the Office of Naval Research (N00014-88-K-0239). The NMR instrumentation was provided through a grant from the Department of Defense. J.L.W. is a Department of Education Fellow.

(11) Haw, J. F.; Richardson, B. R.; Oshiro, I. S.; Lazo, N. D.; Speed, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2052.

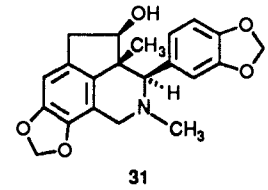
Additions and Corrections

Total Synthesis of (±)-14-Epicorynoline, (±)-Corynoline, and (±)-6-Oxocorynoline [*J. Am. Chem. Soc.* **1983**, *105*, 2873]. MARK CUSHMAN,* AZIZ ABBASPOUR, and YASH PAL GUPTA

In 1988, the isolation and characterization of 13-epicorynoline was reported (Zeng, W.; Liang, W.; He, C.; Zheng, Q.; Tu, G. *Phytochemistry* **1988**, *27*, 599). The spectroscopic data of this natural product did not match that of our earlier prepared synthetic compound **31**, which had been assigned a structure identical with that of 13-epicorynoline. An X-ray analysis of **31** has indicated that the previously assigned structure is incorrect. Since **31** was prepared by $LiAlH_4$ reduction of **30**, structure **30** as given in the publication is also incorrect. The correct structures of **30** and **31** are shown below. Since these compounds were not on the synthetic pathway to the natural products listed in the title, the synthesis of the title compounds is still valid.



30



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Book Reviews

Second Quantized Approach to Quantum Chemistry. An Elementary Introduction. By P. R. Surjân (Chinoin Pharmaceutical and Chemical Works Ltd.). Springer-Verlag: New York and Berlin. 1989. xii + 184 pp. $79.50. ISBN 0-387-51137-7.

The purpose of this book is to make the second-quantized approach accessible to chemists. By discussing a number of topics that ordinarily are not encountered in a standard course of quantum chemistry, Surjân helps to bridge the gap between chemists and physicists. However, this is a very thin book that should be a bit thicker.

Surjân assumes that the reader is familiar with basic quantum mechanics and has a good working knowledge of quantum chemistry, including σ–π separation, Hückel theory, spin orbitals, antisymmetrization, Slater determinants, the Slater–Condon rules, Hartree–Fock theory, and projection operators. Chapters 1–5 introduce the particle-number representation, creation and annihilation operators (and their anticommutation relations), particle-number operators, the second-quantized representation of operators, and the evaluation of matrix elements. The particle-hole formalism is introduced, although it is not used in the book. These chapters are rather terse; additional explanation would be very useful in several places. However, most students should be able to work through them and thereby obtain a working grasp of the second-quantized approach.

The remainder of the book purportedly shows the utility of second quantization in treating a number of chemical problems. In most cases the author is content to develop equations, without much explanation of their significance.

Some parts of the book are confusing, probably because of the author's brevity. At the end of Chapter 8, Surjân shows that the use of incomplete basis sets leads to some mathematical inconsistencies. However, the reader is told nothing about their practical consequences, or how to get around them in actual calculations. In Section 10.4, students will be confused by the sudden insertion of extra electron-interaction terms to convert the electronic Hamiltonian into the Fockian. The discussion of quasi-particle transformations in Chapter 16 contains too many gaps to be very useful to inexperienced readers.

The book contains some inconsistencies. In Chapter 7, Surjân employs commutators rather than anticommutators for Fermion creation and annihilation operators. In developing the second-order density matrix, he uses a unitary transformation between basis functions and Hartree–Fock orbitals. This implies that the creation and annihilation operators for the latter anticommute, just like those for the basis functions. However, the desired result cannot be obtained by using that anticommutation. The development of the Brillouin theorem in Chapter 11 is confusing because basis functions and Hartree–Fock eigenfunctions are not differentiated.

Several chapters are quite interesting. Chapter 10 shows that second quantization provides a very neat path to the particle-hole symmetry relations in alternant π-electron systems. Chapter 13 is a concise discussion of the difficulties encountered with non-orthogonal basis sets. The chapters on the Hellmann–Feynmann theorem and intermolecular interactions are really thought-provoking. Unfortunately, not enough space is devoted to any topic. However, the careful reader will gain a modicum of familiarity with second quantization, and may then be able to understand papers where more complete discussions are given.

John C. Schug, *Virginia Polytechnic Institute and State University*

Laser Micro Analysis. By L. Moenke-Blankenburg (Martin-Luther-University). Wiley-Interscience: New York and Chichester. 1989. xvi + 288 pp. $69.95. ISBN 0-471-63707-6.

This monograph (Volume 105 in the Chemical Analysis series of monographs) discusses the use of laser-based techniques for analysis of materials, with the term micro implying the emphasis on high-spatial resolution through the use of tightly focused laser beams. The principal methods discussed are optical emission spectroscopy and mass spectrometry. The most sensitive of these methods can provide ppm detection limits while using only picograms of the sample. These analytical methods, coupled with laser excitation, are illustrated through a large number of referenced applications (tabulated references make up one-third of the book). The broad overview of this important topic will be useful to most beginning practitioners, while the detailed lists and tables

of applications will guide the reader to the most relevant example systems.

The overall organization of *Laser Micro Analysis* includes introductory information on laser micro analysis (LMA), background material on lasers in general, specifics of the laser/sample interactions which generate the analytical microplasma, and detailed listings of applications of laser-based microprobe methods to different samples. Several recent offspring of the basic LMA methods are also included. Among these are systems coupling laser sampling with microwave plasmas, inductively coupled plasmas, atomic absorbance measurements, or atomic fluorescence measurements. The author has many years of experience in the field of LMA, which itself is one of the earliest applications of lasers, dating to 1962. The historical development of LMA is fully presented. Many of the examples used in the text come from the author's own work, primarily in the 1960s and 1970s. The chapters dealing with the more modern versions of LMA have very current references (to 1988), but several chapters have references limited to the 60s, 70s, and early 80s.

In laser micro analysis, a pulsed laser, typically with approximately 1 *J* of energy per pulse, is used to evaporate picograms to micrograms of material from a solid sample. Emission of light from the gas phase "plasma" sample is detected optically, or sample ions from the plasma are measured via mass spectrometry. In each case identification of the elemental composition of the sample surface is possible. In the optical emission version, high-resolution analysis of the narrow spectral emission lines identifies the elements present, while in the mass spectrometry version, the elements are identified through their characteristic masses. In either case, the initial vaporization step is key, with complex interactions being commonplace, resulting in significant matrix dependencies and concerns about precision.

A single cautionary comment should be noted by purchasers of this volume. The introductory chapter on lasers is not recommended to scientists new to the field. A number of the examples used in this chapter are clearly outdated (1970), and several factual errors appear. However, given the wide availability of introductory laser reference materials, this weakness in the *Laser Micro Analysis* monograph is a minor one.

Jack K. Steehler, *Roanoke College*

Mathematical Methods in Chemistry and Physics. By M. E. Starzak (State University of New York at Binghampton). Plenum: New York and London. 1989. x + 651 pp. $69.50. ISBN 0-306-43066-5.

This book is intended to be a textbook for a rigorous course on matrix-based methods in chemistry and physics. As such, it would perhaps be more appropriately titled "Matrix Methods in Chemistry and Physics". Within its intended scope, however, Starzak's text is outstanding in both its depth and breadth. The first four chapters are devoted to the mathematical basis of matrix techniques. The author covers both the basics and more advanced material of vectors, function spaces, and matrix manipulations. He also devotes an entire chapter to similarity transformations and projections which are central to the determination of the eigenvalues and eigenvectors for a given set of equations. The last seven chapters are then devoted to many illuminating applications of matrix techniques to important physical problems, including examples from normal mode analysis, kinetics, statistical mechanics, quantum mechanics, fluctuation theory, perturbation theory, and group theory. It is my opinion that this latter approach—instruction through a variety of interesting examples—is probably the best way to structure a course in mathematical methods. This style of presentation should also be invaluable to researchers who wish to employ a matrix technique to solve a particular physical problem.

There are two items which would have been strengthened the book if they had been included. First, I think a chapter on numerical methods for solving matrix eigenvalue/eigenvector problems would be quite useful since few realistic problems have analytic solutions. Indeed, most students and researchers use "canned programs" for this purpose, so it would be of value to actually teach them about the techniques they are using on the computer. My second criticism addresses the way in which the applications are presented in the book. More specifically, why not give some illustrative references at the end of each applications chapter? I am sure that many interested readers would enjoy some further reading on the fascinating topics covered in the last seven chapters.

While I would not base a mathematical methods course solely on matrix problems—it should also contain material on partial differential equations, complex analysis, integral equations, integral transforms, the calculus of variations, probability and statistics, and diagrammatic perturbation theory—Michael Starzak's book would make an outstanding supplemental text for such a course. Alternatively, it would be an excellent primary text for a special topics course on matrix methods. Certainly, I also recommend this fine book as an addition to the bookshelf of any researcher in the chemical or physical sciences.

Gregory A. Voth, *University of Pennsylvania*

The Nuclear Overhauser Effect in Structural and Conformational Analysis. By David Neuhaus (MRC Laboratory of Molecular Biology) and Michael Williamson (Roche Products Limited). VCH: New York. 1989. xxii + 522 pp. $95.00. ISBN 0895-73343-9.

The last 20 years have seen several major and well-publicized advances in NMR spectroscopy, including imaging, and high-resolution solid-state and 2D techniques. Less well-publicized has been the increased use of the nuclear Overhauser effect (NOE) in NMR to solve structural and conformational problems. This development has accompanied the widespread use of Fourier transform techniques, high-field superconducting solenoids, increases in computing power, and improvements in instrument sensitivity and stability. The 2D NMR revolution has also contributed greatly to the increased interest in the NOE as a structural tool.

The current work is a comprehensive treatment of the use of the NOE for structural and conformational analysis of organic molecules and biopolymers. It is the first since the classic monograph written by Noggle and Schirmer in 1971. Hence the appearance of the current work is timely and should be well appreciated by researchers who use NMR spectroscopy for structure elucidation. The book is divided into three parts, dealing with theory, experimental practice, and an illustrative review of applications of the NOE to problems in chemistry and biochemistry. The treatment is in-depth with many detailed and clear discussions of particular experiments, limitations, and pitfalls. The important 2D NOESY experiment is covered at length. Many practical aspects of NOE-based experiments are well addressed. The theory section of the text contains a relatively large number of equations, an unfortunate fact of life for proper understanding and application of a technique as sophisticated as that based on the NOE. For the less mathematically inclined, the authors admirably supplement these equations with numerous graphs describing the behavior of various important parameters. Applications to specific systems are subdivided into rigid molecules, flexible molecules, and biopolymers. The descriptions of techniques and applications cover through 1986, with perhaps a half-dozen references in 1987. Thus the most recent developments in this burgeoning field, such as 3D experiments, are not included.

However, this text provides a solid base for examining the more recent literature as well as getting into the business of using the NOE. Nuclear Overhauser enhancement experiments still cannot be classed as routine; their profitable application requires a significant investment of time and energy. This book keeps that investment at a minimum. The reader is advised to have some familiarity with multipulse and 2D NMR. The book is recommended for NMR spectroscopists, chemists, and biochemists who plan to use the NOE to determine molecular structure or conformation.

Richard A. Komoroski, *University of Arkansas for Medical Sciences*

The Handbook of Environmental Chemistry. Volume 4. Part B. Air Pollution. Edited by O. Hutzinger (University of Bayreuth). Springer-Verlag: Berlin and New York. 1989. vii + 261 pp. $117.90. ISBN 0-387-50915-1.

The subject of environmental chemistry is one which literally draws daily headlines in the newspaper. It has entered the parlance of campaigning and noncampaigning politicians. The clergy exhort us to learn about and get involved in environmental matters as a matter of morality. To those of us who have worked in areas which lie within or which border on the subject of environmental chemistry, this attention must be regarded as a happy turn of events. The authors of the contributions in this volume not only have made excellent contributions to the technical literature, but I also derived a sense of satisfaction from language which exhorted the reader, sometimes subtly and sometimes not so subtly, to get concerned about their particular subject and the subject of environmental chemistry as a whole. The idea of a continuing handbook on the subject is timely and fills a need which will continue to grow.

The present volume is one in a series that has expanded beyond its originally intended three-volume limit. In addition, each volume is to be regarded as open-ended, i.e., each volume consists or will consist of more than one part (Parts A, B, etc.). I must admit that I was not familiar with this series when I received this volume to review. I attribute this failing to the great pressure we all face to read more and more materials. This is particularly the case when one works in an area such as environmental chemistry which touches on many different fields. I am pleased that writing this review prompted me to visit the library and familiarize myself with the total series.

When I first read the titles of the contributions to this volume, which has the subtitle *Air Pollution*, I was surprised to find a number of subjects, which most of us would immediately associate with the subject of air pollution, not listed in the contents. I soon learned that Volume 4, Part A, handled some of these topics and others are covered in earlier volumes. In my opinion many readers would find it helpful to have a

listing of the topics covered in all volumes inserted in each volume. The current volume does have an afterleaf which lists the contents of Volume 2, *Reactions and Processes*, but this was not helpful to me when I pondered the apparently missing attention to subjects of some importance to *Air Pollution*.

The book consists of five contributions: Peroxyacyl Nitrates (J. S. Gaffney, N. A. Marley, and E. W. Prestbo), Semivolatile Organic Compounds in the Atmosphere (R. Harkov), Arctic Haze (G. E. Shaw and M. A. K. Khalil), Air Pollution and Materials Damage (F. W. Lipfert), and Air Pollution Control Equipment (H. Brauer). The presentation is readable, complete, and current (I noted some 1988 references). A large amount of useful data is presented.

My overall impression of this volume is very favorable. It will not only serve as a handbook, as the title implies, but could also serve as a textbook in courses on air pollution or as part of a larger sequence on environmental chemistry. I was annoyed by some aspects of the presentation, however. I feel that the series would benefit from some organizational changes. There are no chapters or chapter numbers for example. There is no subheading organization. As currently presented it is difficult to refer to a section or subsection in the same or another volume by a number or number–letter combination in the conventional manner. This omission interferes with one of the important aspects of this developing series. As the series grows this problem will become more acute. Finally, the volume has far too many typographical errors. I began to keep a list of them but decided that this general comment would have to suffice. The current situation in this area is unacceptable.

Robert W. Murray, *University of Missouri—St. Louis*

Foams and Biliquid Foams-Aphrons. By Felix Sebba (Virginia Polytechnic Institute). John Wiley & Sons: New York. 1987. v + 231 pp. $62.95. ISBN 0471-91685-4.

The author uses a very interesting title for his book, a book which addresses a subject that is important to many diverse disciplines. This importance is accompanied by a pressing need to have a book that explains the basic physical–chemical principles of foams and foam behavior in general, and then extends these principles to the understanding of specific types of foams and foam processes. The author points out in his introductory chapter "...the absence of any book on the fluid–fluid interface at a level sufficient for the novice in the field to acquire enough of the fundamentals of the subject to understand the important phenomena which occur at the liquid–gas and liquid–liquid interfaces". The author then goes on to add that the book is multidisciplinary and is not intended to be a monograph on the subject. This latter point is stated to be the reason the number of references are reduced to a minimum. However, this scarcity of recommended readings is a severe limitation for the general effectiveness of the book and defeats one of the author's stated objectives for writing the book, namely, to inspire the novice to pursue this subject further.

The author uses the first three chapters (Introduction, Forces Operating at Interfaces, and Thin Liquid Films) to introduce the reader to the basic concepts relevant to an understanding of the subject matter that is to follow in later chapters. These concepts are written in a logical and concise manner. However, in order to reinforce comprehension of the subjects presented in these chapters, the novice may feel the need to consult the traditional treatment of this material as it is found in physical chemistry texts. The extent to which the novice or general reader will acquire the necessary perspective from these introductory chapters, to comfortably proceed on to the subjects that follow, will be a function of their interest in, and their previous experience with, foams.

In Chapters 4–8, the author begins by suggesting the term "aphrons" be employed to eliminate any confusion with other similar systems such as "bubbles" or "emulsions". It is in these chapters that the author introduces the reader to a concept that is continuously emphasized throughout the book. This concept concerns the role of a specific structural feature of foams that is inherent in the definition of the aphron: "a phase bounded by an encapsulating soapy film". The existence of this encapsulation is important since it is a feature common to all the subsequent structural variations of aphrons, such as colloidal gas aphrons, biliquid foams, polyaphrons, invert aphrons, and microcluster aphrons. The author describes any foam system as having three distinct phases, each with their specific interfacial boundaries. This description represents a departure from the conventional treatment of foams even though multicomponent systems or protective emulsions have been described along these lines.

Chapter 5 treats colloidal gas aphrons, described as very small gas bubbles having special properties, one of which is their unusual stability. The aqueous phase surrounding these gas bubbles differs from the aqueous matrix in which the bubbles are dispersed. Chapter 6 presents the details by which oil spreads on water and discusses the similarity of this system to surface tension characteristics observed in living systems. Chapter 7 introduces biliquid foams. These are foams in which a liquid internal phase or core is surrounded by a thin aqueous lamella that is embedded in a continuous matrix. These biliquid foams can have the internal phase and continuous phases either similar to or different from each other, but irrespective of the particular makeup, the core will be encapsulated, just as in the gas–liquid aphrons. Chapter 8 discusses polyaphrons. These are biliquid foams, wherein an oil droplet, as the internal phase, must be in the appropriate size range and must contain a small amount of surfactant. The author compares polyaphrons to emulsions, emphasizing the difference to be the encapsulating thin film of the internal phase. This is a lengthy chapter which discusses many characteristics of polyaphrons such as their visual appearance, their dispersion, and related thermodynamics. Chapters 9–11 present information on the specific applications of gas bubbles, colloidal gas aphrons, and polyaphrons. Much of this information will be very appropriate for chemical engineers but could have a limited interest to readers from other disciplines. This is also true for the material in Chapter 13, which deals with unusual forms of aphrons, specifically, solid aphrons. Chapter 12 introduces invert aphrons. These are globules of water encapsulated by a membrane made up of aphrons. The author considers these systems to be a model for the semipermeable membrane in biological systems. This theme of modeling is continued in Chapter 14, Biological Significance. The author discusses in this chapter how the behavior of living systems can be related to the forces resulting from surface tension differences. This is followed by a chapter on cancer in which the author proposes that the abnormal behavior of cells is a function of interfacial forces and surface tension. The author contends that this approach suggests a possible route in the search for a cancer cure. Finally, in Chapter 16, there is an interesting artistic application for the patterns that can be produced by the spreading of oil on water.

Without question, many individuals will find this book to be interesting reading. However, the professional scientist who is serious about the study of the physical chemistry characteristics of foams is likely to be disappointed, and in addition, many of these readers may question the value gained by adopting the nomenclature proposed by the author. Since the author admits that much about which he has written is controversial, it would have been beneficial to the reader to have other points of view mentioned wherever appropriate. However, the author's observations and views presented in this book will stimulate discussion among individuals who have any degree of interest whatsoever in foams.

Marion B. Rhodes, *University of Massachusetts at Amherst*

Optimal Structures in Heterogeneous Reaction Systems. Edited by Peter J. Plath (Universität Bremen). Springer-Verlag: Berlin and New York. 1989. vii + 195 pp. $42.00. ISBN 0-387-51573-9.

This monograph was inspired by the Eighth Winter Seminar at Zeinisjoch in the Austrian mountains, which was held from February 27 to March 3, 1988. It is not the proceedings of this workshop, but rather a compilation of some of the essential contributions presented there, together with others describing the basic features of "optimal structures in heterogeneous reaction systems". The book, which consists of eight chapters, was published as Volume 44 of the Springer Series in Synergetics, the general editor of which is Hermann Haken.

In the first chapter, Plath discusses cellular automata models of heterogeneous catalysis with a rather naive application to carbon monoxide oxidation on supported palladium. Then Imbihl gives an excellent review of kinetic oscillations in the carbon monoxide oxidation reaction on single-crystalline surfaces of platinum. Avnir et al. then give a rather simplistic account of the optimization of the structure of heterogeneous catalysts for fractal and nonfractal systems. In the fourth chapter, Zumofen et al. present an excellent overview of hierarchical models in diffusion-limited reactions, including both continuous-time random walks and ultrametric spaces. Then Schuster gives an interesting account of optimization and complexity in molecular biology and physics with a brief discussion of spin glasses (simulated annealing) and a more lengthy account of biological evolution (genetic algorithms). In the sixth chapter, Rössler presents an enchantingly droll discussion of explicit observers which culminates in a "proof" of the Kantian philosophy that the world is objectively different from the way in which it is perceived. In the final two chapters Ebeling et al. and Bestehorn et al. discuss various aspects of pattern processing, formation, and recognition, which include a number of illustrative examples and applications.

The common thread that ties the monograph together is stated in its title, and given the fact that this is a rather fragile thread, the book is probably as successful as one could have expected. It should serve as a useful reference source for the selected, specific topics that it covers—especially for a novice seeking an entree to the field.

W. Henry Weinberg, *University of California, Santa Barbara*