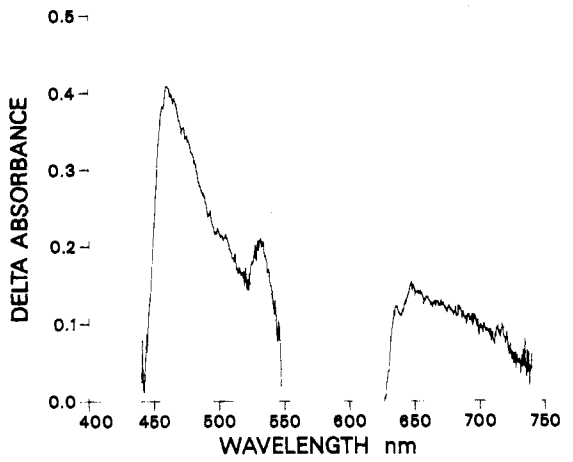

Figure 2. Changes in absorbance of a 2.6×10^{-4} M solution of ZnTPPNQ in toluene/2% pyridine at 100 ps following a 0.6-mJ, 2-ps, 600-nm laser flash. Cell pathlength, 2 mm. Filters that reject stray excitation light cut out the 550–620-nm wavelength region, while the sharp cutoff at 440 nm is due to the intense absorption of the porphyrin Soret band at 419 nm.

The transient absorption spectrum that is observed 100 ps after excitation of ZnTPPNQ in toluene with a 2-ps, 600-nm laser pulse is shown in Figure 2. This transient spectrum possesses single exponential, wavelength-independent rise and decay times of 25 and 370 ps, respectively. The <50-ps lifetime of S_1 in ZnTPPNQ leads us to conclude that the transient we are observing is not an S_1 to S_n absorbance. Measurements of ZnTPPNQ at times >5 ns exhibit no transient absorbance changes, which shows that no long-lived ZnTPP triplet state is formed.

We assign the transient absorption spectrum shown in Figure 2 to the $ZnTPP^+NQ^-$ radical ion pair, since it is very similar to the published spectrum of $ZnTPP^+$.[13] Specifically, the molar extinction coefficient for $ZnTPP^+$ is 3.3×10^4 at 460 nm and 10^4 at 650 nm,[13] while that of NQ^- is 3.2×10^3 at 460 nm and 800 at 650 nm.[14] Thus, the $ZnTPP^+$ spectrum strongly dominates Figure 2.[15] Our evidence is consistent with a simple model in which S_1 decays to a charge-separated state in 25 ps followed by nonradiative decay of this state to ground state in 370 ps.

The quantum yield of $ZnTPP^+NQ^-$ formation was measured. A 2.6×10^{-4} M solution of ZnTPPNQ in toluene was excited with 1.5×10^{15} photons over a sample of volume of 0.015 cm^3. The fraction of the photons absorbed by the sample was determined by measuring the energy of the excitation light incident on the sample and that which passed through the sample. Ignoring the few percent of the photons reflected by the 2-mm path length sample cell, 46% of the photons were absorbed by the sample. Thus, 7.0×10^{14} molecules were excited. The absorbance change in Figure 2 and the molar extinction coefficient for $ZnTPP^+$ at 460 nm yield 5.5×10^{14} $ZnTPP^+NQ^-$ species produced per flash, or a 79% quantum efficiency.

Our results show that *π-stacked geometries are not necessary* for very rapid, efficient electron-transfer quenching of porphyrin singlet states. Moreover, for a given known set of donor–acceptor distances and relative geometries as exemplfied by the series of molecules presented here, photoinduced electron-transfer reactions remain sensitive to both the exothermicity of the electron transfer and the dielectric properties of the medium. A question yet to be addressed is the role of the hydrocarbon spacer as a possible transmission line for the electron transfer.

Acknowledgment. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract W-31-109-Eng-38.

Supplementary Material Available: NMR and visible spectroscopic data for TPPAQ, TPPNQ, and TPPBQ (2 pages). Ordering information is given on any current masthead page.

(13) Fajer, J.; Borg, D. C.; Forman, A.; Dolphin, D.; Felton, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3451–3459.

(14) Afanas'ev, I. B.; Polozova, N. I.; Samokhvalov, G. I. *Zh. Org. Khim.* **1976**, *12*, 2536–2541.

(15) Since ϵ for ZnTPPNQ ground-state absorption is <1000 over the entire wavelength range depicted in Figure 2, the transient difference spectrum shown is a good approximation to the absorption spectrum of the observed transient state.

Book Reviews

Human Biochemistry. By Wilhelm R. Frisell (East Carolina University School of Medicine). Macmillan Publishing Co., Inc., New York. 1982. IX + 845 pp. $35.00.

This textbook has been written for the medical student engaged in his first course in biochemistry, a one-semester course dealing with the fundamentals of human biochemistry. To achieve his stated purpose, the author has made a unitary presentation of human biochemistry within the contexts of the background and of the intended career practices of the first-year medical student-eventually-physician. Since the chemical background of his student is limited while career application is extensive, the text is dominantly verbal, chemical theory and chemical structure being limited to essentials and mechanism non-existent. If the latter are faults, this reviewer does not so consider them in view of the book's purposes; they are to a certain extent remedied by the adequate problem and answer sections of the book.

To achieve a coherent presentation, the author follows a short introductory section entitled General Consideration (Unit I), Part I, Basic Biochemistry (Units II through VII), and Part II, Metabolic Basis of Human Biochemistry (Units VIII and IX). Units II through VII detail the elements of molecular and cellular biochemistry, proteins and their enzymatic function, bioenergetics, carbohydrate metabolism, lipid metabolism, nitrogen metabolism, replication, and expression of genetic information. Units VIII and IX are entitled Compartmentation of Metabolic Activities—Tissue and Organ Interrelationships and Regulation—Balance and Imbalance in Human Metabolism, respectively.

Each unit consists of several chapters, at least, allowing a relatively full exploration of the unit. Unit VIII contains nine chapters, ranging from Chapter 25, Compartmentation of Metabolic Systems and Transmembrane Transport, to Chapter 33, Biochemistry of Vision, with organ and tissue biochemistry in between. Unit IX contains four chapters with topics ranging from metabolic controls to elements of nutrition. Parts I and II are about equal in allotted pages. Part II is particularly well documented with schema, diagrams, structures, and illustrations.

The appendix contains useful physicochemical tables of units and abbreviations, a glossary, as well as a quite complete table, alphabetically arranged, of "normal" ranges of the constituents of body fluids. In addition the appendix contains an answer section to the problems found at the end of each chapter. The answers are informative and instructive and anchor the students' knowledge.

In a textbook of voluminous detail but not of exaggerated length, errors of osmission, in particular, and errors of commission are bound to occur. The reviewer noted several. The equation (page 19) for the oxidative decarboxylation of pyruvic acid lacks oxygen as a reactant; the international unit (IU) of enzyme activity is mentioned but not defined; the tail-to-tail fatty acid membrane model is not depicted; and the use (page 19) of proposed reaction intermediates to model biochemical reactions is questionable. The mitochondrion in its ultrastructure is not depicted except as part of a striated muscle fiber (page 506) and there the label is incorrectly positioned.

This reviewer considers the book within its stated purposes a formidable one, one to be recommended to the usually bright medical student

capable of absorbing and digesting large amounts of mental food in a short period of time. This book is also to be recommended to the student in biochemistry. It provides in its units VIII and IX, 323 pages, a relevancy of facts about the biochemistry of man.

Oscar Gawron, *Duquesne University*

Tools of the Mind. By V. Stibic (formerly of Philips Industries Ltd., Eindhoven, The Netherlands). North-Holland Publishing Co., Amsterdam. 1982. xiii + 297 pp. $35.00.

This book, given its title and subtitle "technique and methods for intellectual work", could have been about a variety of subjects. The book is concerned with tools in the sense that they are aids. The techniques and methods involve how an individual may employ modern technologies to assist in the collection, organization, and transmission of information. One chapter deals with personal planning and accounting; however, the main thrust of the text is that the use of modern technologies can often be helpful in enabling an individual to make more effective use of his time. That this is the case seems almost self-evident. What this reviewer found more interesting were the suggestions and examples of how procedures which are often associated with organizational or managerial structures can and should be used by individuals.

The emphasis is on the use of modern devices such as word processors, pocket calculators, electronic mail, personal computers, etc. This text will not help a potential user of these devices to make choices from among the hardware and software which is available. Rather it might help the person unfamiliar with the possibilities opened up by modern technology to assess whether he can or should begin to use these technologies. Appropriate attention is paid to the important question of matching the technology to the task. The low key, but persuasive style of this book is much more appealing than the "gee whiz" approach of much material available on personal computing.

The basic premise of the author is that we often do not think of how we organize and carry out our personal tasks but that we should. He is successful in presenting this message. Those who are using modern technology may find some new and interesting suggestions; those who have been reluctant to give up time tested methods might conclude that there is something to be gained by using the new technologies.

Stephen Z. Goldberg, *Adelphi University*

Advances in Chemical Physics. Volume 54. Edited by I. Prigogine (University of Brussels and University of Texas) and S. A. Rice (University of Chicago). John Wiley and Sons, New York. 1983. ix + 485 pp. $75.00.

This volume of the series continues the tradition of the earlier volumes, that is "...to have experts present comprehensive analyses of subjects of interest, and to encourage the expression of individual points of view". In meeting this aim, it constitutes a strong link in a long chain of reviews and research reports that address the fundamental aspects of chemical physics.

Volume 54 is comprised of four chapters. The first by J. Olsen, D. L. Yeager, and P. Jorgensen, is entitled Optimization and Characterization of a Multiconfigurational Self-Consistent Field (MCSF) State, and it addresses the problem of finding the most direct procedure for carrying out MCSF calculations starting from a variety of characterizations of a multiconfigurational state and the development of efficient and reliable optimization procedures. A lengthy appendix provides a discussion of redundant variables and a variety of functions required in the procedures discussed in the main text of this contribution.

The chapter by my colleague L. Goodman and his student R. Rava, on Two-Photon Spectroscopy of Perturbed Benzenes, provides not only the theoretical framework required for understanding the unique features of the spectra of aromatic molecules but also a wealth of experimental data pertaining to these systems as well. In addition to the two-photon spectrum of the parent benzene, the effect of isotopic labeling is also comprehensively discussed. The pronounced deuterium-labeling effects on two-photon spectra have no counterpart in the traditional UV spectra. The authors provide a level of understanding comparable to that for traditional spectra, and to this end, regularities and systematics of the details of the spectra of toluene, the monohalobenzenes, and a number of related molecules are considered and discussed in the context of the transitions allowed in the two-photon excitation of these aromatic species.

The third chapter, Inhomogeneous Relativistic Electron Systems: A density-functional Formalism, by M. V. Ramana and A. K. Rajagopal, concerns itself with an examination of the relativistic effects which can be observed in the description of the allowed energy states of atoms and molecules. The introduction consists of an extensive review of the earlier work on relativistic effects in many-election systems and makes the subsequent discussion of the Formal Theory very much easier to handle than might at first glance have been expected. A brief appendix details some of the mathematical steps utilized in the main discussion and addresses the question of the equivalence of some of the expressions for the dielectric constant which have been reported in the literature.

The final contribution, by J. M. Turlet, Ph. Kottis, and M. R. Philpott, entitled Polariton and Surface Exciton State Effects in the Photodynamics of Organic Molecular Crystals, will be of major interest to investigators studying the spectroscopy of molecular crystals. It details the results of a new experimental study of the reflectivity and fluorescence of anthracene at very low (1.6 K) temperatures. The discussion offerred by these authors benefits from a detailed introductory review of bulk and surface excitons in molecular crystals, the effect of exciton–photon coupling, and related topics, which make the subsequent discussion of the results on anthracene more readily accessible to the general reader. There is a well-illustrated discussion of experimental methods as applied to the study of anthracene, followed by a detailed presentation of the new experimental results. The 252 references reflect the care with which the authors have addressed the topic.

In summary, this volume provides a detailed discussion of four topics in the broad field of chemical physics and deserves to be high on the acquisitions list of most chemistry research libraries. Whether it will be viewed as a required addition to the personal libraries of chemical physicists will be a decision based on the overlap between the topics covered and the interests of the potential purchaser and the magnitude of his/her book budget.

R. H. Herber, *Rutgers University*

Catalyst Manufacture. By Alvin B. Stiles (University of Delaware). Marcel Dekker, Inc., New York. 1983. iv + 176 pp. $49.75.

Professor Stiles has written a reference book on the manufacture of catalysts based on his many years of experience in catalyst research and application to plant operations. The text gives typical flow sheets for the most common catalyst preparations. Each of the standard processes used is discussed briefly, and the text is illustrated with photographs of much of the equipment used. The last half of the book is dedicated to a presentation of the preparation procedures for a number of the more typical, industrial catalysts (such as zeolites, oxidation catalysts, supported precious metal catalysts, etc.).

Since the science of catalyst preparation is not really addressed, this text may not be particularly useful in an academic laboratory. However, it would be a useful reference to industrial chemists and chemical engineers, or anyone else, seeking to prepare large quantities of catalysts for pilot plant studies or for commercialization. The description of the pertinent processes, equipment, and potential difficulties will be particularly useful. Certainly, it is very important to be aware of differences resulting from "mass production" of catalysts as opposed to preparation of small quantities in the research laboratory. Professor Stiles cautions that catalysts prepared and used on a small scale may be quite different from those prepared on a large scale and undergoing densification and particle forming operations.

Finally, this text and copies of "Design of Industrial Catalysts" by D. L. Trimm (Elsevier Scientific Publishing Company, New York, 1980) and "Handbook of Catalyst Manufacture" by M. Sittig (Noyes Data Corp., Park Ridge, NJ, 1978) would provide a useful set of reference books for those engaged in or contemplating the design and manufacture of industrial catalysts.

James G. Goodwin, Jr., *University of Pittsburgh*

Mathematical Methods in the Physical Sciences. 2nd Edition. By Mary L. Boas. John Wiley & Sons, New York. 1983. xx + 793 pp. $32.95.

This volume treats mathematical procedures of importance to juniors, seniors, and graduate students, with the presupposition that the students have had a single year of freshman calculus. The emphasis of the author has been on developing and explaining results in a clear way. The language is that of a series of well-prepared lectures, given by someone who recognizes that modern students are not trained to see the logical implications of an assertion. For self-study by students at the intended level, this is clearly the best-written text I have ever seen. Major topics include infinite series, complex numbers, vectors, matrices, calculus of several variables, fourier analysis, the calculus of variations, tensor analysis, ordinary and partial differential equations, special functions, complex analysis, integral transforms, and probability. The text is enhanced by many worked examples and homework problems, roughly half of which have solutions provided. For students with specific questions, or as the basis for a sophomore–junior year course in mathematical methods, this volume is highly recommended.

George D. J. Phillies, *The University of Michigan*