

Book Reviews *

Advances in Electron Transfer Chemistry. Volume 4. Edited by Patrick S. Mariano (University of Maryland). JAI Press: Greenwich, CT. 1994. ix + 215 pp. \$97.50. ISBN 1-55938-506-5.

As is evident from the title, this book is the fourth in a series of monographs dealing with electron transfer processes. Like its predecessors, the topics presented in this book are timely and up-to-date in terms of literature coverage and are written by individuals who are recognized experts in their respective fields. For the most part, the contributing authors have provided reviews which are focused and illustrative, rather than comprehensive, and which contain a fair portion of their own work. Overall, the book provides an excellent introduction to recent advances in the field of electron transfer and would provide easy entry into the primary literature for anyone interested in learning more. Both the quality of the presentations and overall coverage of the volume make it a "must" for acquisition by academic libraries. The modest cost of the book should also make it an attractive addition to many personal libraries.

The first chapter of the book by F. Saeva (Eastman Kodak) deals with the photoinduced electron transfer (PIET) chemistry of sulfonium ions. This chemistry has practical application because it provides a means of photochemically generating acids for use in photoresist and other technologies. In this chapter, *intramolecular* PIET in aromatic sulfonium ions is discussed ($\text{Ar}-(\text{spacer})-\text{SR}_2^+$, where Ar serves as the chromophore which, after excitation, transfers an electron to the sulfonium ion portion of the molecule). An intermediate singlet radical cation/alkyl radical pair ($\text{Ar}-(\text{spacer})-\text{SR}^{\bullet+}/\text{R}^{\bullet}$) is envisioned. Issues such as the role of the spacer, effect of distance, etc., are discussed. Overall, the chapter is well-written and easily understood but somewhat short and limited in scope.

The next chapter by K. S. Peters (University of Colorado) also deals with PIET and reviews both theory and experiment pertaining to electron transfer from a donor molecule (D) to an excited state acceptor (A^*). The competition between long-range electron transfer yielding solvent-separated radical ion pairs (SSRIP), short-range electron transfer yielding contact radical ion pairs (CRIP), and the dynamics of interconversion between SSRIPs, CRIPs, and free ions are discussed. The chapter provides an insightful overview of nearly 30 years of work in the field starting with the seminal work of Rehm and Weller and continuing through to the present time, with ample results and observations from the recent literature. A particularly interesting aspect of the chapter comes near the end where the author is careful to point out discrepancies between theory and experiment (where they exist) and makes several specific suggestions regarding issues that future studies in the field should address.

The third chapter, authored by J.-M. Savéant (de l'Université de Paris), deals with the dynamics of dissociative electron transfer, e.g., $\text{A}-\text{B} + \text{e}^- \rightarrow \text{A}^{\bullet} + \text{B}^-$ (or $\text{A}^- + \text{B}^{\bullet}$), and the distinction between concerted and stepwise pathways (i.e., is $\text{A}-\text{B}^{\bullet-}$ an intermediate?). For the concerted pathway, Savéant presents a theory for describing the relationship between the activation barrier and driving force for the process, based upon a relatively simple modification of Marcus-Hush theory which incorporates a term accounting for the bond dissociation energy of $\text{A}-\text{B}$. Examples of both heterogeneous electron transfer (i.e., at an electrode surface) and homogeneous electron transfer are discussed in the context of this model. Most of the examples cited involve dissociation of alkyl, aryl, or benzyl halides. The chapter begins with a theoretical discussion of electron transfer in the context of Marcus-Hush theory and recent modifications thereof followed by experimental results (primarily from electrochemical studies) which lend support to the proposed model. Several examples are provided which demonstrate how the theory might be used to estimate important thermodynamic data (bond dissociation energies, radical stabilization energies, electrochemical potentials, etc.). The use of the symmetry factor (α) as a diagnostic criterion for electron transfer occurring in a concerted (bond cleavage concurrent with electron transfer) vs stepwise (radical anion intermediate) fashion is discussed. At the end of the chapter, some insight is provided into the factors mitigating whether the concerted vs stepwise pathway is followed from a structure/reactivity perspective. This chapter is extremely detailed, reviews a large amount of theoretical and experimental data in the field, and is not "light

reading" by any measure. An interested reader would need to be fairly conversant with electrochemistry (in addition to physical chemistry) in order to derive maximal benefit from this chapter. However, the effort would be rewarded as this chapter is a gem.

The final chapter of the book is a combined effort by U. C. Yoon (Pusan National University), P. S. Mariano (University of Maryland), R. S. Givens (University of Kansas), and B. W. Atwater, III (Bell Communications Research). The chapter provides a thorough and critical review of photoinduced electron transfer from amines to appropriate excited state acceptors (arenes, ketones, enones, etc.). The review begins with a general discussion of PIET and quickly moves on to a discussion of the redox properties of amines and the chemistry of amine cation (aminium) radicals and of aminyl and α -amino radicals (the products of N-H and α -C-H deprotonation, respectively). The central (and major) portion of the chapter focuses on the descriptive SET photochemistry of amines with respect to N-H and α -C-H deprotonations and other fragmentation pathways (e.g., decarboxylation, desilylation). The chapter concludes with a detailed discussion of the mechanistic photochemistry associated with reactions of tertiary amines and α,β -unsaturated ketones, which nicely compliments the Peters chapter. A few minor errors were noted in the schemes (e.g., pentavalent carbon), but these were readily recognizable and did not seriously detract from the overall effectiveness of the presentation.

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The Picture Book of Quantum Mechanics, 2nd Edition. By Siegmund Brandt and Hans Dieter Dahmen (Siegen University). Springer-Verlag: New York, Berlin, and Heidelberg. 1995. xviii + 423 pp with 486 illustrations. ISBN 0-387-94380-3.

The title of this book is somewhat misleading, as I expected it to feature illustrations of wave functions, probability distributions, etc., for several simple quantum mechanical systems with at most a cursory treatment of the underlying mathematics. While such pictures are indeed to be found throughout the book, many of the fundamental principles of quantum mechanics are presented in considerable mathematical detail. Indeed, the level of sophistication is probably too advanced for the book to serve as a first-semester course in quantum mechanics for graduate students in chemistry. However, I would recommend it as a supplementary reference for motivated and well-prepared students, as its emphasis on visualization is pedagogically effective.

The book is broken up into four major sections. Chapters 1-3 serve as an introduction to quantum mechanics in which the usual topics are discussed (electron diffraction, photoelectric effect, and the Stern-Gerlach experiment) followed by a nice presentation of the properties of wave packets and the classical uncertainty principle. The Schrödinger equation and the Heisenberg uncertainty principle are also introduced. In these early chapters as well as throughout the book, the authors do a laudable job of discussing both correspondences and distinctions between quantum and classical mechanics. Chapters 4-6 focus on the quantum mechanics of both bound and scattering states of one dimensional systems, while two-dimensional coupled harmonic oscillators are treated in Chapters 7-8. At this point, the notion of indistinguishability is introduced along with the exclusion principle. Chapters 9-14 treat scattering and bound states in three dimensions, including an excellent section on the hydrogen atom that features several beautiful pictures of orbitals viewed along selected two-dimensional "cuts". The treatment of angular momentum in Chapter 9 is thorough and—like the discussion of the hydrogen atom—strengthened by figures that communicate shapes and probability distributions of angular momentum eigenfunctions in a clear way. Chapter 15 introduces the phenomenon of spin, and the final chapter discusses experimental examples that are mostly of interest to physicists.

For the most part, I think that *The Picture Book of Quantum Mechanics* is more of a physicist's book than a chemist's book. This should not be regarded as a criticism, since both authors are physicists and have likely targeted the subject matter to that field. Chemists might be disappointed that many-electron wave functions are considered only

*Unsigned book reviews are by the Book Review Editor.

for atoms; even then, unfamiliar language is used (for example, Hartree–Fock theory for atoms is referred to as the shell model). The only discussion of molecules in the book appears in Section 16.4, where the infrared spectra of normal alkanes are discussed. However, this is not a standard treatment in terms of stretching and bending vibrations and normal coordinate theory. Rather, vibrational spectroscopy is used to illustrate resonance scattering of a photon by the probed molecules. While one may interpret the experiments in this way, the perspective is probably unfamiliar to most chemists. The lack of emphasis on chemistry and molecular quantum mechanics is perhaps most clearly seen by glancing through the index at the end of the book. Here, one finds references to “charm quark”, “electron-positron annihilation”, “pion-proton scattering”, and the “Y particle”; while no entries are found for “molecule”, “molecular orbital”, “Born-Oppenheimer approximation” or any kind of molecular spectroscopy apart from that mentioned above.

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Femtochemistry. Ultrafast Dynamics of the Chemical Bond. Volumes 1 and 2. By Ahmed H. Zewail (California Institute of Technology). World Scientific Publishing Co.: London. 1994. xxix + 917 pp. Vol. 1: \$60.00. ISBN 9810217366. Vol. 2: \$53.00. ISBN 9810217382.

Albert Einstein first proposed the idea of the laser in 1916. However, it was not until 1960 that Theodore Maiman (Hughes Laboratories) demonstrated the first successful laser based on a synthetic ruby rod. Thirty years of development has taken the laser from a novelty to the state of the art with advances in laser power, wavelength selectivity, and time resolution. Today's lasers offer wavelengths from the ultraviolet to the infrared, powers capable of cutting through metal, and time resolution from the steady state to the femtosecond time scale (10^{-15} s). The advent of femtosecond time resolution has opened the door to reaction dynamics offering a way to probe a chemical process from reactants through the transition state to products.

This two-volume set contains 13 chapters providing a thorough look at the development of femtosecond laser spectroscopy including the state of the art techniques available for probing reaction dynamics. Volume 1 begins with a historical perspective on the development of femtosecond laser spectroscopy. Several introductory articles provide reviews of concepts and methodology including discussions on transition state dynamics and the role of alignment and orientation. The next collection of articles discusses the fundamental aspects of femtosecond transition state spectroscopy including the theoretical analysis of the experimental observable $I(t, \lambda)$ and the relationship to potential energy surfaces. The ultrafast techniques are then applied to elementary and complex reactions including methyl iodide fragmentation and hydrogen atom transfer reactions. A series of articles focus on solvent dynamics, nonreactive systems, ultrafast electron diffraction, and chemical dynamics. Volume 2 begins with a chapter on reaction rates including discussions of photofragmentation, photoisomerization, and structural effects on reaction dynamics. The concept of intramolecular vibrational energy redistribution (IVR) and rotational coherence are discussed including the experimental approach and the theoretical analysis which provides the link to time-resolved molecular structure determination.

The first 12 chapters are a compilation of almost 70 articles, most of which are also published elsewhere. The last chapter provides an extensive list of the author's publications organized by topic extending over his career at CalTech from 1976 to 1994.

This two-volume set provides an excellent source of information on the state of the art in femtosecond spectroscopy. It is an invaluable reference for experts in the field as well as those interested in mastering the experimental and theoretical aspects of ultrafast time-resolved spectroscopy.

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Micelles, Monolayers, and Biomembranes. By Malcolm N. Jones (University of Manchester) and Dennis Chapman (Royal Free Hospital School of Medicine, London, England). Wiley-Liss: New York. 1995. xii + 252 pp. \$48.00. ISBN 0-471-56139-8; 0-471-30596-0 (paperback).

This short textbook will be useful to a wide audience and provides a description of many applications of lipids in self-aggregated structures such as micelles, monolayers, and bilayers. Although the primary emphasis is on the behavior of phospholipids in monolayers, micelles, and liposomes, many applications involving membrane proteins are also presented.

The book consists of 10 chapters of approximately 25 pages each: amphiphathic molecules (detergents, bile salts, sterols, fatty acids, phospholipids, glycolipids); physical chemistry of monolayers and micelles; phase behavior of aqueous dispersions of phospholipids; preparation and properties of liposomes, including application for their use in drug delivery; binding of detergents to water-soluble proteins; arrangements of proteins and glycoproteins in biomembranes; membrane transport and receptor functions; protein translocation; and dynamic motions of membrane components.

The book is not intended to serve as an in-depth text. Although the book is well written, unfortunately it does not present a modern view of how membranes operate. Structure–function relationships are poorly presented, and some of the discussions of interesting recent developments in membrane research such as receptors, clathrin binding, cell–cell contacts, and second messenger functions of membrane components are superficial. Almost all of the references listed at the end of each chapter are to work prior to the mid-1980s, and throughout the book, many important references are omitted; for example, the pioneering work of McConnell and of Möhwald on monolayer fluorescence microscopy is not referenced. Nevertheless, the book would serve as a useful introductory text for undergraduate-level courses in chemistry, physics, and materials science which seek to provide a general overview of the field of amphiphathic molecules and an introduction to the study of membranes.

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NMR Techniques in Catalysis. Edited by A. T. Bell and Alexander Pines (University of California at Berkeley). Marcel Dekker: New York. 1994. viii + 432 pp. \$165.00. ISBN 0-8247-9173-8.

This book is an effort to examine the role NMR spectroscopy plays in catalysis. The focus of the book is heterogeneous catalysis, rather than catalysis in general. As the editors state in the introductory chapter, “rather than aim for a comprehensive review of NMR and catalysis, the present volume allows several leading practitioners to describe examples of materials and processes in heterogeneous catalysis under investigation by NMR techniques.” That is what is presented: after an introductory chapter, there are presented chapters on zeolites, molecular diffusion, in situ NMR, bulk oxide studies, silica and alumina surfaces, and new techniques. Each chapter is a review, with extensive emphasis on the work of the author(s) of that chapter. Because of length, the chapters tend to be more nearly complete than papers found in publications that collect symposium papers in a bound form. Nevertheless, this volume “feels” like a symposium volume—its style, the choice of topics, and the way in which contributions to the various areas are presented.

The papers in the volume fall into roughly two categories: (a) ones that emphasize how typical NMR parameters give insight into structural and dynamic aspects of the physics of a molecule at a surface of some nominally catalytic material and (b) ones that, while still focusing on aspects of NMR technology and surface physics, emphasize the reactivity of the catalytic process and how NMR fits into the larger picture of the catalytic activity of the material. In this second category, the article by Haw particularly clearly demonstrates to a chemist interested in the chemical changes transpiring in a catalytic system how NMR might provide insight into mechanisms and chemistry.

For what the editors have set out to do (provide a limited set of papers on applications of NMR spectroscopy to several topics in surface chemistry), this is an interesting volume. However, unless one were specifically interested in several of the topics addressed and in the work of the particular authors, the expense of the volume makes it difficult to justify purchase.

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