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BOOK REVIEWS

Advances in Chemical Physics. Volume 121. Edited by I. Prigogine (University of Texas at Austin and Université Libre de Bruxelles) and S. A. Rice (University of Chicago). J. Wiley & Sons: New York. 2002. x + 558 pp. $175.00. ISBN 0-471-20504-4.

This volume contains seven individual reviews, which, in the spirit of this classic series, cover a broad range of topics in chemical physics. Because these topics are not directly related, the chapters are individually reviewed below.

Chapter 1, "Ultrafast Dynamics and Spectroscopy of Bacterial Photosynthetic Reaction Centers" by Lin, et al., describes the construction of a microscopic model Hamiltonian and uses it to derive expressions for absorption spectra, microscopic rates of electron transfer, energy transfer, radiationless transitions, relaxation dynamics, ultrafast dynamics, and pump-probe spectra. These expressions are used to calculate and then compare with experimental phenomena such as vibrational relaxation processes, quantum beats, and the dynamics of electronic processes from femtosecond time-resolved spectra. Overall, the chapter is well written, comprehensive, and useful, but there are a few errors in the figures, and the derivations are sometimes choppy. The references are comprehensive and up-to-date.

Chapter 2, entitled "Polymer Melts at Solid Surfaces" by Yethiraj, presents the application of theoretical and computational models in the liquid state to the behavior of polymers at surfaces. Monte Carlo simulations of density profiles of polymers at solid surfaces are calculated and compared to both integral equation and density functional models derived within this chapter. In most cases, density functional theory is consistent with the simulations. Unfortunately, no experimental data are provided for comparison. A particularly nice feature of this chapter is the section on future directions for this line of research. There are only a few references from 2000 and later, however, suggesting that some of the conclusions may be somewhat out-of-date.

Chapter 3, "Morphology of Surfaces in Mesoscopic Polymers, Surfactants, Electrons, or Reaction−Diffusion Systems: Methods, Simulations, and Measurements" by Aksimentiev, Fialkowski, and Holyst, is a comprehensive presentation of the theoretical tools used to define, identify, and quantitate surfaces. Part I of this chapter provides a basic introduction, Part II describes the theoretical tools for specific systems, and Part III is devoted to numerical and analytical computations of general surface characteristics. This chapter examines a wide range of physical phenomena that span the entire range of chemistry, from electrons to cellular organelles, and provides a comprehensive reference list, including Internet links and free software available from the authors for the morphological analysis of 2-D and 3-D surfaces.

In the fourth chapter, Henri-Rousseau and co-workers present "Infrared Line Shapes of Weak Hydrogen Bonds: Recent Quantum Developments". The theoretical formalism is clearly presented and includes important recent developments. The review relies somewhat on the knowledge of an earlier review from the authors, and most recent references are to their own work.

Chapter 5, entitled "Two-Center Effects in Ionization by Ion-Impact in Heavy-Particle Collisions" by O'Rourke, McSherry, and Crothers, provides a nice comparison of theory and experiment in single ionization processes during ion-atom collisions. Briefly, both continuum-distorted-wave and continuum-distorted-wave eikonal-initial-state models are described quantitatively and then used to model experimental results from complementary recoil-ion momentum and ejected electron spectroscopies. This well-written chapter does an excellent job of highlighting the significant similarities and differences between theory and experiment, even for the nonexpert, and shows a lack of support for the controversial saddle-point ionization mechanism for electron emission from collisions of protons with H_2, helium, and neon. Most of the important references are from the late 1990s and early 2000s, making this survey very timely.

In Chapter 6, "Evolution Times of Probability Distributions and Averages − Exact Solutions of the Kramers' Problem", Malakhov and Pankratov describe approaches for obtaining exact-time characteristics of Markov processes. The authors give a good introduction to the basic theory of random processes and present a wealth of formal tools for the study of the time-characteristics of transition processes. This review provides up-to-date references and will be useful to theorists interested, for example, in transition rates in the context of chemical and biochemical reactions.

In the final chapter, "Ab initio Quantum Molecular Dynamics", Ben-Nun and Martinez give an excellent introduction to ab initio approaches to molecular dynamics. The authors stress the need for the development of methods to treat nuclear degrees of freedom through quantum mechanics and set the stage for their proposed approach, the ab initio multiple spawning method. The fundamental equations of the method are clearly presented along with the approximations required for practical implementations. The authors conclude with an outlook on the future applicability of their promising approach and the various challenges at hand. The references are thorough and place the review in the context of contemporary research in quantum molecular dynamics. This chapter is a great source for anyone interested in learning about ab initio molecular dynamics.

In summary, this volume follows the excellent tradition of the series and provides a very useful reference for researchers interested in keeping up with advances in the numerous facets of research in chemical physics.

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Unsigned book reviews are by the Book Review Editor.

Quantitative Millimeter Wavelength Spectrometry. By John F. Alder (UMIST, U.K.) and John G. Baker (Manchester University, U.K.). The Royal Society of Chemistry: Cambridge. 2002. xiv + 122 pp. ISBN 0-85404-575-9.

This monograph addresses chemical analysis using millimeter wave spectrophotometry, a very specialized topic that has been around for a long time but is beset with technical difficulties. It utilizes a region of the electromagnetic spectrum in which very narrow absorption lines can be observed so that problems arising from the overlapping of lines from different components of a mixture can be avoided. However, this occurs only in the gas phase at low pressures, absorptions in condensed phases being so broad as to be impracticable for analytical work.

In an opening chapter, the authors summarize those aspects of the theory of microwave spectroscopy that are needed for analytical applications. They then focus on cavity spectrometers and appropriate sources and detectors for millimeter wave spectrometry. The technicalities are described very clearly, and sufficient detail is given to provide an excellent guide for scientists entering this very special aspect of analytical chemistry. Such scientists would need a much stronger background in physics and instrumentation than in chemistry, however.

The authors' presentation is very much a personal account of the particular choices they have made in their own efforts to build an analytical spectrometer. In places, they are rather too ready to dismiss alternatives. For example, Stark modulation is rejected without making any persuasive argument against it (the reviewer's research group has operated a viable analytical cavity instrument for years based on Stark modulation). It is also doubtful whether the attention given to analysis at atmospheric pressure is warranted. Line widths at one atmosphere are such that there is little hope of achieving satisfactory analyses of gaseous mixtures with the possible exception in which one component is a very small polar molecule in an otherwise nonpolar mixture.

The two following chapters review previously published attempts to develop a commercially viable analytical spectrometer and summarize the authors' own attempts in this direction. The latter chapter contains many useful comments and practical tips that are not found in the research literature.

A concluding four-page chapter entitled "The Future for Quantitative Millimeter Wavelength Spectrometry" offers valuable thoughts on the problems to be faced in developing an analytical instrument. It ends with some speculation on various technical developments that could lead to the desired kind of instrument in the future. However, one discerns some wistfulness on the part of the authors because they have not yet succeeded in producing the object of their desire after many years in the field.

The question remaining for this reviewer when confronted with this well-written and constructed small monograph on a very specialized subject is "Who will buy it?" A tiny group of scientists who might wish to enter the field might purchase it and maybe a few others, out of general interest. Large science libraries should have copies, but the financial stringencies of these days may mean that libraries will be reluctant to buy it.

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Guidelines for Achieving High Accuracy in Isotope Dilution Mass Spectrometry (IDMS). Edited by Mike Sargent and Rita Harte (Laboratory of the Government Chemist, Teddington, U.K.) and Chris Harrington (De Montfort University, Leicester, U.K.). Royal Society of Chemistry (for the Laboratory of the Government Chemist): Cambridge. 2002. vi + 50 pp. $54.95. ISBN 0-85404-418-3.

This book provides simplified guidelines on the use of isotope dilution mass spectrometry (IDMS) for high accuracy measurements and gives detailed methodologies for both organic and inorganic IDMS. It contains the following five chapters: (1) "Introduction" (which covers the advantages and disadvantages of IDMS); (2) "The Principles of IDMS"; (3) "Critical States and Sources of Error"; (4) "The Structured Approach to IDMS Analysis"; and (5) "Optimized Spiking for Inorganic IDMS Analysis". The book concludes with three appendices that provide lists of references and additional reading, a glossary of terms and abbreviations, and a list of standard IDMS equations.

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Applied Electrospray Mass Spectrometry. Practical Spectroscopy Series. Volume 32. Edited by Birendra N. Pramanik (Schering-Plough Research Institute, Kenilworth, NJ), A. K. Ganguly (Stevens Institute of Technology, Hoboken, NJ), and Michael L. Gross (Washington University, Saint Louis). Marcel Dekker: New York and Basel. 2002. viii + 434 pp. $185.00. ISBN 0-8247-0618-8.

This well-edited volume presents two chapters that introduce electrospray ionization mass spectrometry (ESI-MS) and emerging techniques for "nanoflow" electrospray and nine chapters on their applications. Of the latter, three chapters are devoted to advanced applications of electrospray that, although impressive and clearly presented, are probably still too specialized to be used by nonexperts. These include the use of Fourier transform mass spectrometry for rapid and quantitative proteomics, detection of noncovalent complexes of proteins (with a short section on complexes of nucleic acids), and ESI-MS studies of protein structure and dynamics by H/D exchange. Although the remaining chapters are more descriptive than instructional, they should be more directly useful to scientists interested in how ESI-MS can be used for the analysis, characterization, or pharmacokinetics of small-molecule drugs, for combinatorial chemistry, or for peptide and (glyco)protein analysis. All chapters are well supported by current references, all of which, commendably, include article titles.

The first chapter, "Electrospray Ionization Mass Spectrometry: History, Theory, and Instrumentation" by Cody, is easily the most useful one in the book; even readers who are mainly interested in a specific application covered in one of the later chapters should read this first. Although it may not seem that the "history, theory, and instrumentation" of electrospray would deserve much coverage in a book devoted to applications, the author is careful to observe an applied context, leaving more technical details to nearly *500* references. For example, historical discussion of the development of electrospray interfaces for higher flow rates provides a framework for later descriptions

of the desolvation process and ultimately helps the reader understand how to select an appropriate ESI source. Electrospray theory is discussed in just enough depth to elucidate the practical consequences of the ionization process, including applicability to different classes of analytes, limitations of dynamic range, compatibility with solvents and buffers, and the formation of multiply charged ions. A discussion of sensitivity is followed by the admonition that reports of very low "sample consumption" usually do not mean that very low *concentrations* were measured and that "practical detection limits depend on how easily one can handle small [volumes] of sample." This chapter also includes an excellent discussion of the strengths and weaknesses of the five main types of mass analyzers. A section on mass calibration, resolving power, and accurate mass measurements is supported by a very useful appendix that lists monoisotopic masses for 11 different series (clusters or polymers) of calibration compounds. The chapter concludes with a discussion of mathematical techniques for "deconvoluting" mass spectra containing multiple charge states of the same analyte, and an explanation of why this is a misnomer.

The second chapter presents a similarly useful historical perspective on the development of "nanoflow" electrospray sources, including spray tips packed with chromatographic stationary phases. Although its coverage of these important recent developments is not comprehensive, this chapter nicely explains the concepts of concentration- versus mass flow-sensitive response and further illustrates the importance of considering the entire sample-handling protocol for analyses that require high practical sensitivity. Additional reinforcement of this point—which may be the most important single idea in the book—is provided by the final chapter, on the combination of microdialysis sampling with "microelectrospray" sources for neuropeptide and drug analysis. This chapter also clarifies the nomenclature most commonly used for different types of low flow sources.

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Advances in Dendritic Macromolecules. Volume 5. Edited by George R. Newkome (University of Akron). JAI Press, Inc. (An Imprint of Elsevier Science): Amsterdam, London, New York, Oxford, Shannon, Tokyo. 2002. xii + 256 pp. $136.00. ISBN 0-7623-0839-7.

This volume is part of an ongoing series that aims to summarize advances in the field of dendrimers, an area of increasing importance both fundamentally and from the perspective of its applications. The book succeeds admirably in reviewing four aspects of this broadening field and generally provides references through the year 2000, with a few from 2001.

Azobenzene-containing systems are the focus of the first chapter by McGrath and Villavicencio. They describe syntheses and photoresponsive properties of both flexible and rigid dendrimers with a single azobenzene moiety at the cores or up to six at the peripheries; these investigations were carried out in their labs. They also describe work from other labs that concerns dendrimers with up to 64 azobenzene moieties at the periphery.

In the next chapter, Gitsov discusses the syntheses and characterization of linear-dendritic block copolymers of various overall architectures and complexities. Dendrimeric species [poly(benzyl ether), poly(amidoamine), polypropyleneimine, and polysilane structures] attached to linear polymers [polystyrene, poly(ethylene oxide), polybutadiene, polyarylenes, polyamides] as end groups, cores, or as side chains are described (in some contradiction to the chapter's title).

The following chapter by Astruc and co-workers surveys dendritic systems containing ferrocene and closely related moieties. It includes syntheses by both convergent and divergent approaches to systems with up to 243 ferrocene units on the peripheries. Sensor and battery applications are briefly addressed.

Wiener and Narayanan discuss the application of dendrimers in magnetic resonance imaging in the final chapter. A thorough description of the MRI experiment and the theory associated with metal-ion-promoted proton relaxation is followed by an overview of experimental results for small molecule gadolinium complexes and dendritic analogues in terms of relaxation times, biological targeting, and metabolic fate. This chapter will be of value to those interested in MRI in general because of its thoroughness.

Overall, this volume is a necessary acquisition for up-to-date science libraries and a very useful information source for those interested in dendrimer syntheses, properties, and applications.

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Topics in Current Chemistry 221. Contrast Agents I: Magnetic Resonance Imaging. Edited by Werner Krause (International Project Management Therapeutics, Schering AG, Berlin). Springer-Verlag: Berlin, Heidelberg, New York. 2002. x + 250 pp. $159.00. ISBN 3-540-42247-1.

Magnetic resonance imaging (MRI) is now firmly entrenched as one of the most widely used and versatile imaging modalities in diagnostic medicine. Some diagnostic exams are aided considerably by contrast agents (CAs), which typically are small paramagnetic complexes that alter the relaxation characteristics of tissue water. This short review is intended to provide an update of progress in the development of such agents. The editor suggests in the preface that progress in MRI was only possible due to the concurrent development of CAs. Although it is true that CAs continue to play an important role in this technology, the majority of diagnostic MRI exams are still performed without the administration of a CA. Thus, it may be historically more accurate to suggest that advances in MRI, which have largely been driven by advances in magnet technology and faster computers, have motivated chemists to understand the physical principles involved in CA design and efficiency better. Most commercial CAs are based on gadolinium complexes, so it has been interesting to observe how developments in MRI technology have catalyzed and invigorated the basic field of the chemistry of lanthanide complexation. Much of this is at least touched upon in this review.

It is unfortunate that this short, readable book follows by only a few months a more comprehensive review of this same subject (*The Chemistry of Contrast Agents in Medical Magnetic Resonance Imaging*; Merbach, A. E., Tóth, É., Eds.; Wiley: New York, 2001. Reviewed: *J. Am. Chem. Soc.* **2002**, *124*, 884). In fact, most of the authors who contributed to *Topics in Current Chemistry 221* also contributed to this earlier book.

The first chapter provides a very general introduction to gadolinium complexes and the basic principles governing their use as contrast agents. Chapters 2−4 and 7 are well written and cover the most important aspects of complexation chemistry, dynamics, and relaxation theory. They are, however, mini-versions of chapters covering similar topics in the Merbach and Tóth book. Chapter 5, covering new classes of CAs, nicely summarizes recent advances in targeted agents and the so-called "smart" agents, complexes that respond to changes in temperature, pH, pO_2, Ca^{2+}, or enzyme activity. This is an exciting new area for future CA development, so this chapter will be of interest to those new to this field. Chapter 6, covering non-gadolinium-based CAs, is unique and informative; it offers a comprehensive review of the less widely studied manganese-, iron-, and copper-based agents. These latter ions are less efficient than gadolinium, but their biological properties might be taken advantage of in the development of next generation "molecular" imaging agents.

In summary, this short book meets its mark as a *Topics in Current Chemistry* review. Although less comprehensive than other reviews on this topic, it offers a nice overview for beginning graduate students and newcomers to the field.

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Inorganic Syntheses: Volume 33. Edited by Dimitri Coucouvanis (University of Michigan). Wiley-Interscience: New York. 2002. xxvi + 276 pp. $90.00. ISBN 0-471-20825-6.

Volume 33 of this classic series contains the following four chapters: "Synthesis of Selected Supramolecules", "Useful Reagents and Ligands", "Solid-State Materials and Clusters", and "Compounds of General Interest". Contributor, subject, and formula indices complete the book.

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