Book Reviews

Molecular Vibrations and Mean Square Amplitudes. By SVEN J. CYVIN, Dr.techn., Institute of Physical Chemistry, Technical University of Norway, Trondheim. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 1968. 424 pp. 17 × 24 cm. $27.00.

It is widely appreciated that the amplitudes of molecular vibrations play a significant role in such diverse and important properties as melting points, kinetic isotope effects, inertial defects in rotational spectra, and intensities in Raman scattering. Nevertheless, the quantitative treatment of vibrational amplitudes has heretofore received scant attention in reference books. Several workers in the fields of diffraction and spectroscopy, most notably James, Morino, and Kuchitsu, had shown how to calculate mean amplitudes from molecular potential energy functions. Considerable impetus was given to the study of amplitudes two decades ago by the Karles' first direct measurements of intramolecular motions by electron diffraction. The first worker to specialize in the treatment of mean amplitudes, however, has been Sven Cyvin, and it is fitting that he should be author of the first book to appear on the subject.

The book's main emphasis is on relatively small gas-phase molecules. Its theoretical development is confined almost exclusively to the idealized problem of small, harmonic vibrations. In the subject of its concentration, the book is comprehensive, exhaustively documented, and accessible. Although its title suggests a kinship with the numerous other existing works on molecular vibrations, a fundamental difference may be discerned, for example, from the well-organized bibliography containing over 800 literature references. These display a minimal overlap with references in conventional treatises and represent most of the articles published through 1967 which describe methods of calculating mean amplitudes or report amplitudes deduced by diffraction or spectroscopy.

The contents of the book include a survey of experimental and theoretical work to date; a development of the theory of molecular vibration in terms of the standard Wilson GF matrix approach, in terms of compliance matrices, and from the standpoint of mean-square amplitude matrices; extensive treatments of individual molecular types with a generous sprinkling of tables of useful relations; compilations of numerical results of mean amplitudes for hundreds of molecules; Bastiansen–Morino shrinkage effects, relationships between Coriolis constants and mean amplitudes, and a forecast of future developments.

The author's style is succinct, often unconventional, but always clear. His virtual neglect in his formal treatments of the ramifications introduced by anharmonicity is not unreasonable, perhaps, in view of the practical difficulty in making quantitative corrections. Nevertheless, he routinely tabulates calculated amplitudes to three or four figures even though the corrected values would frequently differ in the second figure. This troublesome complication should not be allowed to detract from the real virtues of the book. As a meticulously constructed compendium of mean amplitudes, it is an important reference book for workers in many fields. As an original and authoritative treatise on molecular vibrations, it would be a valuable addition to the library of any serious student of the subject.

L. S. Bartell

Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48104

Enzymes in Nucleic Acid Research. By MICHEL PRIVAT DE GARILHE. Holden-Day, Inc., 500 Sansome St., San Francisco, Calif. 1968. 393 pp 18 × 24.5 cm. $16.25.

This book is a revised and expanded edition in English of the French book *Les Nucleases* which was published in 1964 by Hermann, Paris. There are eight chapters which the author in his preface divides into three sections. Chapters V through VIII constitute the third and best section. These chapters, which are the ones that conform in contents to the title of the book, present a detailed account of enzymes that hydrolyze the nucleic acids and their partial hydrolytic products. Here the author is on home territory, and a wealth of information is presented that in the reviewer's opinion makes the book worth possessing. A criticism is that it is sometimes difficult to ascertain the substrate specificity of a given enzyme. In two cases work on the amino acid sequences and spatial structures of enzymes is included (for pancreatic RNAase and T_1 RNAase). The application of enzymes to the determination of nucleic acid sequences is also discussed, and Holley's analysis of the sequences of alanyl-tRNA is very briefly reviewed. Atlhough the author states that the book contains nine chapters, only eight are numbered; Chapter VII seems to be erroneously numbered as Chapter VIII; possibly the massive synoptic tables of nucleolytic enzymes and their properties which follow Chapter VIII could be considered as a ninth chapter.

In spite of slight drawbacks, Chapters V through VIII contain so much more information about nucleolytic enzymes than probably can be obtained from any other single source that students and investigators will no doubt be very glad to have all this material at hand in one place.

The rest of the material, which is covered in Chapters I through IV, in the opinion of the reviewer cannot be as highly recommended. The first section of the book, according to the author, comprises Chapters I, II, and III. Chapter I, which is a section on definition of terms used in describing the nucleic acids and their derivatives, together with formulas and examples, is apparently aimed mainly at beginners. Chapter II is entitled "Nucleic Acids-Basic Concepts." The types, occurrence, molecular weights, and structures of ribonucleic acids are discussed with somewhat uneven emphasis. Some of the material seemed misleading to the reviewer, such as a statement that there is still very little information about the structures of nucleic acids. Also, it might appear from what is said about ribosomal RNA that this possesses a true double-stranded structure, in the same sense that viral replicative phase RNA is double stranded.

The question of the functions of the ribonucleic acids leads to a discussion of protein synthesis which again is unevenly presented and not entirely up to date. The discussing of coding is definitely not up to date and also is subject to misinterpretation. For instance, the statement is made that the problem of code degeneracy has not yet found a satisfactory solution. In the discussion on transcription, the discovery of Hurwitz of the transcribing polymerase seems by implication to be accredited to Chamberlin and Berg.

The third chapter is concerned with the chemical synthesis, biosynthesis, and isolation from tissues of nucleic acids and the chemical synthesis of nucleic acid derivatives. Polynucleotide phosphorylases and the polymerases that form DNA are briefly discussed; mixed DNA–RNA polymers are also mentioned. DNA ligase, however, is not included. In the section of isolation of RNA's and DNA's some obsolete methods are reported in considerable detail, whereas other better ones are only mentioned briefly.

Although a considerable amount of factual material and a very good reference list has been included, Chapter III in the opinion of the reviewer cannot be highly recommended, since it contains a mixture of obsolete and modern information which has not been very well evaluated.

Chapter IV on "Analytical Methods" constitutes what the author terms the second section of his book. The practical spectroscopy of the nucleic acids and their derivatives is discussed briefly; the application of various physical and chemical methods to the separation and determination of bases, nucleosides, nucleotides, and nucleic acids are included. In a short section on methods for determining nucleic acids in tissues, the necessity of separating the hydrolyzed nucleic acids from protein before running color reactions is not made clear. The principal criticism of Chapter IV is that there is too little critical evaluation of the methodology, and detail is presented in some instances that is more or less obsolete.

It would seem to the reviewer that the second and some of the third chapter could have been left out of this book, in view of the much better presentations that can be found elsewhere. The author does not seem at be at home in the fields covered in these chapters. One rather startling statement from Chapter II is that the discovery of the double-stranded DNA structure is the most brilliant single scientific contribution of the 20th century. One would think that general relativity and wave mechanics might at least be considered as close runners up!

With the deletion or drastic revision of Chapter II together with

the revision and strengthening of Chapters III and IV, the book would be less comprehensive but more acceptable in the opinion of the reviewer. The book contains a sprinkling of typographical errors (*e.g.*, Wilkies for Wilkins), but most or all of these seem to be of a trivial nature.

Alexander L. Dounce
Department of Biochemistry
University of Rochester, Rochester, New York

The Mass Spectra of Organic Molecules. By J. H. BEYNON, R. A. SAUNDERS, and A. E. WILLIAMS, Research Department, Imperial Chemical Industries Ltd., Manchester, England. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 1968. ix + 510 pp. 17.5 × 25 cm. $34.00.

The 1960 publication of "Mass Spectrometry and its Applications to Organic Chemistry" by J. H. Beynon gave a strong impetus to this awakening field. Despite the amazing progress since that time in applications of the method, his volume is still used as a standard reference because of its authoritative treatment of basic principles and instrumentation. To update other sections, Dr. Beynon and his colleagues have prepared the present book which is "devoted to a description of the ways in which a wide variety of organic compounds behave in a mass spectrometer." An up-to-date general reference work of this kind would be of high importance for most workers in the field; however, this book appears only a year after one with almost identical objectives written by Budzikiewicz, Djerassi, and Williams (reviewed in *J. Am. Chem. Soc.*, **90**, 3900 (1968)). Unfortunately for the reviewer, the unusually high price of BS+W (twice the price of BD+W) demands a comparison and choice; the average reader will not be satisfied with the conclusion that both are meritorious, although this is indeed true. I am forced to conclude that although BS+W contains much unique and useful information, BD+W is much more complete and up-to-date in its literature coverage, and it is superior in over-all coherence and in the logic and consistency of its mechanistic treatment.

In BD+W the literature is covered through early 1967; in BS+W few references are given after 1965, even to the authors' work, and the over-all coverage is less complete. For example, 12 of the 15 mass spectral references cited in Chapter 19 of BD+W (sulfoxides, sulfones) do not appear in BS+W; this is also true of Chapter 20 (pyridines). However, BS+W is more complete in referencing early work; roughly half its bibliography is dated 1960 and earlier.

I feel that a substantial strength of BD+W is its consistent mechanistic approach to mass spectral behavior which provides a logical, although often unsubstantiated, organization for the multitude of collected empirical facts. BS+W is uncritical and frustratingly inconsistent in this regard; for example, the mechanism on page 166 employs a dashed line, a negative charge, and a lasso to indicate electron density changes, while that on the opposite page uses fishhooks and dots. More seriously, the extensive general discussion of rearrangements (pp 63–79), for which most of the cited references are earlier than 1960, shows no mechanisms with the modern conventions of arrows and fishhooks to indicate electron transfers, or with localized charge or radical sites. Yet the ubiquitous ketone rearrangement is later depicted on page 193 with a fishhook indicating electron transfer *away* from the radical site, and on page 211 for the identical rearrangement in aldehydes the electron transfer is shown as occurring *to* the radical site. No mechanism is shown for many cases in which this might have helped clarify the recited empirical facts, which could be due to a reluctance for speculation where the evidence is not definitive. However, the authors are not consistent in this; their mechanism for the loss of a CO molecule from α-nitronaphthalene (p 338) involves eight separate steps.

This book is generally free from typographical errors, although the incorrect sign in the rings-plus-double-bonds formula (p 25) will cause trouble for the unwary. For no apparent reason the pages of my copy were randomly printed on two different kinds of paper (glossy and matte finishes). Otherwise the printing and binding were of satisfactory quality, although they hardly reflect the astonishing price of nearly 7¢ per page.

Despite the above remarks, I found many parts of this volume enjoyable and rewarding, and most organic mass spectrometrists should also. The book reflects the fact that the combined mass spectrometry experience of the authors far exceeds that found in any other laboratory that I know. The book holds many useful facts, observations, and suggestions which were previously unpublished. The perspective and philosophy of the authors in many matters is interesting and provocative. This is seen in the discussions of spectra of some types of molecules, and especially in the collection of examples of actual problems which they have solved. Descriptions involving instrumentation or physics are in the high tradition of the 1960 volume. It is certainly unfortunate that the credit due to the authors for their talents and efforts must be diluted by the appearance of a more current volume and by the publisher's lethargic production rate and avaricious pricing policy.

F. W. McLafferty
Department of Chemistry, Cornell University
Ithaca, New York 14850

Carbonium Ions. An Introduction. By D. BETHELL, Department of Organic Chemistry, University of Liverpool, Liverpool, England, and V. GOLD, Department of Chemistry, King's College, London, England. Academic Press Inc., Ltd., Berkeley Square House, Berkeley Square, London, W. 1, England. 1967. xii + 387 pp. 16 × 23 cm. $16.00.

The authors indicate in the introduction their intent to fill the "need for a general text in which carbonium-ion chemistry is treated as a whole and which interconnects the various strands of development." Though the multitudinous studies that concern carbonium ions have been partially chronicled in specialized or brief reviews, this is the first volume devoted solely to the role of carbonium ions in chemistry.

Subjects discussed at length include methods of generating carbonium ions; reactions of carbonium ions; physical studies of carbonium ions; kinetic, product, and stereochemical studies of reactions involving carbonium ions as short-lived intermediates; determinations of carbonium ion stabilities by equilibrium and kinetic studies; effects on carbonium ion stabilities of internal structural features and of interactions with solvent and other ions; bridged carbonium ions; and species related to carbonium ions. Though coverage is uneven, most detailed topics that I specifically sought were represented at least by a few lines and a leading reference. Certainly one of the greatest values of this volume will be to give the thorough reader an indication of the wide range of studies which concern carbonium ions. It is a testimony to the surprising vitality of this area of research that some sections already are dated. The book was completed before the Olah torrent reached flood stage and too early to include such significant developments as the application of ion cyclotron resonance spectroscopy to the study of carbonium ions and the extension to protonated aromatic and to alkyl cations of Arnett's studies of heats of formation by solution calorimetry.

Though this volume is relatively free of typographical errors, I thought that some passages, as illustrated by a few examples below, are misleading or fail to indicate significant relationships or reasonable conclusions. The X-ray crystallographic studies that are cited concern ions in which conjugation favors planarity and therefore do not provide the implied (p 4) support for the assignment of planar structures to alkyl carbonium ions. The impression may be fostered (pp 91, 92, and 143) that solvolyses of primary halides generally are Sn1 in character. The spirit of the Curtin–Hammett principle is violated in several discussions (p 265, for example). Some of the possibilities suggested (pp 25–26) for the source of the ultraviolet absorption formed on addition of *t*-butyl alcohol to concentrated sulfuric acid are no longer viable. The insertion reaction of a carbene, though stated (p 295) to lack a direct analogy in carbonium ion chemistry, seems analogous to the formation (p 266) of cyclopropane from the propyl cation.

However, such minor flaws are to be expected in a book that covers so broad an area and do not detract seriously from its value as an introduction to carbonium ion chemistry. It is written at a level that should make it accessible even to advanced undergraduate or beginning graduate students. Most persons interested in learning about this area will want to purchase a copy.

Herman G. Richey, Jr.
Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania 16802

Introduction to the Principles of Heterogeneous Catalysis. By J. M. THOMAS, Department of Chemistry, University College of North Wales, Bangor, Wales, and W. J. THOMAS, Department of Chemical Engineering, University College of Swansea, Swansea, Wales. Academic Press Inc., Ltd., Berkeley Square House, Berkeley Square, London, W. 1, England. 1967. x + 544 pp. 16 × 23 cm. $21.50.

For many years there has been a definite need for a reasonably compact book on heterogeneous catalysis, a subject of fundamental interest in chemical theory and of overwhelming importance in the national economy. For in heterogeneous catalytic systems, we have the "reactive species" whether it be a radical, ion, or complex concentrated at the surface to be examined. On the other hand, every major chemical process is based on catalytic or surface reactions. While there have been a number of treatises and review series on the subject, there have been very few books that attempt to survey the field.

The authors state in the preface: "As teachers of and researches in, surface chemistry and chemical engineering, we have felt the need for a text which concentrates throughout on the *principles* of heterogeneous catalysis. A text in which emphasis is given to the experimental principles as to the theoretical ones; .... It is our conviction that undergraduates and young research workers, to whom this book is primarily aimed, ought to know as much about how the results are obtained as they do about the various theories that unify the results."

The book has nine chapters: a short introductory chapter and then three chapters on adsorption, a chapter on lattice imperfections and one on geometric, electronic, and related factors. The chapter on Dynamics of Catalysis uses adsorption as an approach, and the last chapter is on design of catalytic reactors. The mechanism of some typical heterogeneous reactions surveys the whole field in 80 pages.

From the authors' point of view the "Principles of Heterogeneous Catalysis" seem to be the principles of adsorption and mass transfer. The material presented deals with scientific catalysis rather than theoretical catalysis. The experimental techniques stressed are those of a physicist rather than that of a physical chemist. Modern physical techniques are fully described though their application to catalysis is often not presented. The theoretical treatment is very clear. The book is well written and very useful. However, it does not disclose the principles of catalysis. In the reviewer's opinion we still have to find them. The subject of catalysis is still an art rather than a science.

John Turkevich
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Collisional Activation in Gases. By BRIAN STEVENS, M.A., D. Phil., Department of Chemistry, University of Sheffield, England. Pergamon Press Inc., 44–01 21st St., Long Island City, N. Y. 1968, xi + 236 pp. 15.5 × 23 cm. $14.00.

Stevens' book does a quite good job of updating Cottrell and McCoubrey's book through 1964, and includes some references as recent as 1965. It is more an indication of the rate of progress in the area than a criticism of the author to note that the book's treatment of the theory of energy transfer processes is already definitely dated; also the author has omitted discussion of some work which in this reviewer's opinion should have been included (energy transfer calculations by Benson and his coworkers, and Nikitin's work on nonadiabatic vibrational relaxation, for example). Some of the theoretical sections are marred by poor proofreading and other errors which will make the book less useful to students than it might otherwise be; such errors are found on pages 8, 12, 23, 25, 41, 42, 45, 46, 47, 52, 58, and 60, for example. The labeling and caption of Figure 4.10 seem to imply that the whole is less than the sum of its parts. The discussion of unimolecular rate theory (Section 4.8) does not take into account the significant advances made by R. A. Marcus and his coworkers.

Despite these shortcomings the book is a useful contribution to the literature, giving good discussions of a broad selection of experimental methods and presenting theoretical discussions of these techniques at a level accessible to the student in roughly the first or second year of graduate study. The subjects covered in the book are indicated by the chapter headings: energy transfer in gas reactions; theoretical treatments of energy transfer processes; experimental methods based on relaxation techniques; experimental methods involving rate measurements of competing processes; interpretation of experimental data for low energy levels; energy transfer from higher vibration levels. The book closes with a very comprehensive tabulation of experimental data.

David J. Wilson
University of Rochester
Rochester, New York 14627