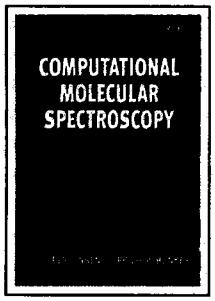
Computational Molecular Spectroscopy



By Per Jensen and Philip R. Bunker. John Wiley & Sons, New York 2000. 670 pp., hardcover € 219.00.—ISBN 0-471-48998-0

A book that claims to be the first to present a "comprehensive treatment" of a subject, namely the theoretical calculation of high resolution molecular spectra, raises high expectations, especially since the editors are both known experts in this field. The 20 chapters are wisely arranged in five parts, and are based on the Born–Oppenheimer approximation, which is treated by the editors in the first, short chapter. This approximation defines potential energy surfaces of electronic states. The investigation of these surfaces is the subject of the second part of the book, beginning with Chapter 2.

The second chapter (Császár, Allen, Yamaguchi, Schaefer) deals with the ground state surfaces of small molecules, and offers an outstanding and lucid review of current ab initio techniques and their limitations. This text can be highly recommended as a general overview for readers interested in quantum-chemical methods.

The following two chapters get more specific about the calculation and analysis of intermolecular interaction energies (Moszynski, Wormer, van der Avoird), and about density functional theory and its application to ZEKE spectroscopy of small transition-metal-containing clusters (Bérces, Zgierski, Yang). Both texts include a fairly short introduction to the underlying theories and experimental techniques. The fifth chapter, on electronically excited states (Buenker, Hirsch, Li, Gu, Alekseyev, Liebermann, Kimura), lacks such an introduction. The examples describing small molecules should have been preceded by a more precise description of multireference and CI methods, which would have complemented the description of ground state methods in Chapter 2.

A more detailed introduction to the basic treatment of relativistic effects (spin–orbit coupling, ECPs) is presented in the sixth chapter (Hess, Marian), illustrated by some examples which are discussed thoroughly. In the concluding chapter of this part, Sauer and Packer describe the calculation of molecular properties such as electric and magnetic moments, leading to predicted NMR shieldings and spin–spin coupling constants.

In the third part of the book, the energy surfaces are used to approximately describe rotational–vibrational states. After introducing the classical method using an effective Hamiltonian H_{eff} in the first chapter (Sarka, Demaison), the following one by Tennyson deals with calculation of spectra by the variational method, in which an initially assumed surface is fitted iteratively to reproduce the experimental spectroscopic parameters. When a high density of states or strong rotation–vibration interactions are present, the approach using local modes can replace the use of normal coordinates, as is shown by Halonen for some main group hydrides.

The next three chapters discuss clusters and larger molecules, even proteins. The SCF approach for coupled anharmonic vibrations is presented by Gerber and Jung, then vibrations with low frequencies (large amplitude motions) are discussed by Makarewicz. These occur, for example, in van der Waals complexes, and can be separated from the normal vibrations which have higher frequencies. The current status of spectroscopic research on small water clusters is presented as an application in Chapter 13 by Wales.

The familiar image of potential energy surfaces is left behind in the fourth part of the book. In some cases the Born–Oppenheimer approximation breaks down and nonadiabatic coupling between different electronic states has to be considered. Yarkony's treatment of diatomic molecules is very precise, and makes greater demands on the reader's knowledge of quantum mechanics than other chapters. The Renner effect, which is the interaction between rotational-vibrational states at points where the electronic wavefunction is degenerate, is discussed in Chapter 15 by the editors, then the same effect is treated by the effective Hamiltonian approach in Chapter 16 (Brown). Electronic degeneracy is also the cause of the Jahn–Teller effect which, together with spin–orbit coupling, can distort vibrational energy levels (Barckholtz, Miller).

An alternative to the precise theoretical determination of energy levels is the simulation of the time dependence of molecular motion. Wavepacket and molecular dynamics treatments are the theoretical tools relevant to time-resolved laser spectroscopy experiments, and are dealt with in the last part of the book. In Chapter 18, Child describes semiclassical wavepacket methods, which lead from classical phase space to quantum-mechanical eigenvalues. In Chapter 19 (Seidemann), some methods of wavepacket dynamics are presented together with a number of practical examples, ranging from excited iodine to charge transport in semiconductors. The book is completed with a chapter by Tse and Rousseau about Car–Parinello molecular dynamics. Values of macroscopic observables such as absorption coefficients are obtained by the evaluation of correlation functions from the calculated trajectories.

In summary, the book certainly meets the goal at which it aims. Although limited to the calculation of rotational and vibrational spectra, it contains a comprehensive presentation of theoretical molecular spectroscopy. The combination of theory and illustrative examples is very well balanced in most chapters, and the extensive index adds to the positive impression. Readers

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such as graduate students or senior researchers may use it as a valuable source of information during their work in the fields of theoretical chemistry or molecular spectroscopy. Moreover, the vast amount of citations in all chapters stimulates further reading. Nevertheless, a basic knowledge of quantum chemistry and molecular spectroscopy is required from the reader.

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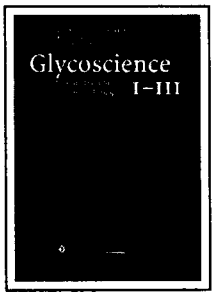
Glycoscience



Chemistry and Chemical Biology. Vols. I–III. Edited by Bertram Fraser-Reid, Kuniaki Tatsuta and Joachim Thiem. Springer-Verlag, Heidelberg 2001. xix + 2854 pp., hardcover € 749.00.—ISBN 3-540-67765-8; version including CD-ROM € 934.00.—ISBN 3-540-67764-X

The editors of this three-volume work of nearly 3000 pages, who are themselves well-known scientists active in the area of carbohydrate chemistry, have invited 90 expert authors from throughout the world to contribute articles intended to give a comprehensive overview of the current situation in the broad field of glycoscience. Starting with monosaccharides and ways of extending and modifying them by classical methods of organic synthesis, the 66 articles cover a wide range of aspects, including oligosaccharides and oligonucleotides, glycobiology, and the physical and pharmacological properties of the synthetic and natural products described. However, the work offers more than an instantaneous snapshot of this very active field of research—it has some of the characteristics of a textbook, not only conveying an impression of the broad scope of the subject but also giving deeper insights.

Volume I is concerned with general principles of saccharide chemistry, beginning with a very long introductory section which describes the occurrence of carbohydrates, their properties and methods for purifying them, and the structures and conformations of furanoses and pyranoses. This is followed by two further sections dealing with reactions at non-anomeric and anomeric positions. The first of these includes articles on reactions using protecting groups, oxidations, reductions, rearrangements, and exchange reactions in which oxygen atoms are replaced by carbon, hydrogen, or heteroatoms. The second describes glycosylation reactions leading to the formation of O-, S-, N-, and C-glycosides.

Volume II begins with a section that is devoted to monosaccharides, first dealing with their occurrence, properties, and importance. The following chapters of this section describe partial and de novo syntheses of these compounds, followed by biosynthesis and breakdown processes, and the genetic and enzymatic aspects of some important metabolic and transport processes. The second section is devoted to oligosaccharides, with the main emphasis on their chemical synthesis (including the solid-phase methods that are still at an early stage of development), and on their central importance in transmitting biochemical signals.

Volume III is mainly concerned with the biological and pharmacological aspects of complex polysaccharides such as heparin, glycolipids that are important constituents of cell walls, and the large class of glycoproteins. Other glycoconjugates are also discussed, including many antibiotics and antitumor agents, and the glycomimetics that are of special pharmacological interest.

In a work containing as many as 66 articles it is inevitable that the contributions vary considerably in their informativeness from the reader's viewpoint. Some of the topics seem rather too specialized, and in a few of the articles the choice of literature citations (of which there are over 9000 in the work as a whole) is not fully representative. Also in many of the articles the literature coverage does not extend beyond 1998. However, these criticisms are more than outweighed by the value of the comprehensive overview provided by this work.

Another minor shortcoming is the absence of a chapter on modern methods for determining the structures of oligosaccharides, which would certainly have fitted very well into the overall scheme. Also the presentation of the structural formulas in many of the chapters leaves much to be desired, and in a few cases oversteps the boundary between unconventionality and near-illegibility. In the appendix listing the 1996 IUPAC recommendations for nomenclature of carbohydrates the quality of printing is very unsatisfactory.

On the whole, however, these three volumes provide, in a useful and pleasing format, an impressively comprehensive and up-to-date overview of the chemistry and chemical biology of carbohydrates. They help the reader to access the accumulated knowledge from over 120 years of research in this area, in a form that nonspecialists too will find useful. A CD-ROM is also available to facilitate searching in the work.

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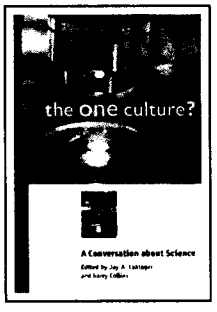
The One Culture?



A Conversation about Science. By Jay A. Labinger and Harry Collins. University Press, Chicago 2001. xi + 329 pp., softcover $ 18.00.—ISBN 0-226-46723-6

Should chemists feel guilty for their indifference to the controversy known as the Science Wars? In the spring of 1996, Alan Sokal, a physicist from New York University, published in *Social Text* a parody poking fun at the cultural studies community. The ensuing debate pitted sociologists of science and their ilk, intent upon defending their field "sociology of scientific knowledge"

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