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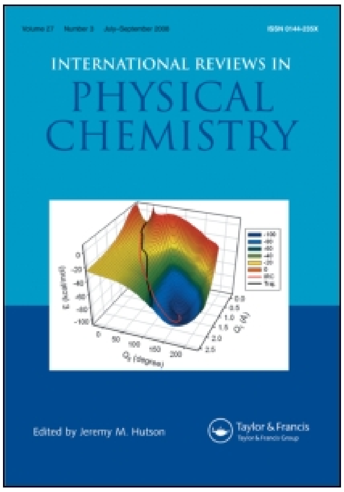

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Book Reviews

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Book reviews

Royal Society of Chemistry Specialist Periodical Reports, Nuclear Magnetic Resonance, Volume 18. Senior Reporter G. A. WEBB (Royal Society of Chemistry, 1989.) [Pp. vi + 511.] £110. ISBN 0 85186 412 0.

This is the 18th volume in a series published annually, and chemists interested in nuclear magnetic resonance (NMR) have grown accustomed to having these volumes on their library shelves, and expect them to continue. It represents a great deal of work on the part of the contributors in classification and referencing, since they aim to cover all the new NMR work published between June 1987 and May 1988. On the whole, these reviews tend to be rather uncritical; indeed it would be difficult to be comprehensive and critical at the same time. Nevertheless, before undertaking work in any new area of NMR, research workers would be well advised to read the relevant RSC Specialist Periodical Report. It is in this reference mode that most people will find it useful; it is hardly a publication for browsing.

As with all cooperative works, the quality varies considerably with the particular author, and these cannot always be the acknowledged experts in the field (they are usually too busy). More subtly, the quality of the entire volume depends critically on the choice of chapter topics, presumably decided by the Senior Reporter. On the whole these choices are wisely made, but if there is a blind spot here, it could be disastrous. Of course, from time to time a whole new area of NMR emerges which does not fit tidily into the existing framework. Similarly, the routine established in previous volumes is propagated throughout the series; for example, almost inevitably the first chapter is on the theoretical aspects of nuclear shielding. It is this insistence on categorizing the subject which could be the most dangerous aspect of this most laudable and long-running project. As one small example, the framework of *Volume 18* seems to preclude anything on magnetic resonance imaging on non-living systems.

This volume has chapters on nuclear shielding, spin–spin coupling, relaxation, solid-state NMR, multiple-pulse methods, macromolecules (natural and synthetic), conformational analysis, NMR of living systems, paramagnetic systems, and liquid crystals. Some chapters (such as the one on NMR of living systems) are in a period of explosive growth, whereas others (such as the theoretical aspects of spin–spin coupling) are quieter subjects. It is conceivable that the former will soon become so important in its own right that it has to be split off from this type of publication altogether. Multiple-pulse NMR is also a rapidly-growing area; in this volume this is taken to include all multidimensional NMR experiments.

This type of book generates much tabular material, often very useful indeed. The section on symbols and abbreviations seemed, however, to be rather out of data. There is a bewildering variety of abbreviations for new pulse sequences in NMR and an up-to-date compilation would have been appropriate and useful, but the ones mentioned here (for example DEFT and PRFT) are very old-hat.

Efforts have clearly been made to keep down costs by using camera-ready copy, and this shows up as slightly different typography in the different chapters. Most readers will welcome this economy measure. Unfortunately, at £110, the price of the book is still very high and must be beyond the pocket of many students and research workers. In the present climate, some libraries may also think twice about a continuing subscription.

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Stereochemical Applications of Gas-Phase Electron Diffraction. Part A: The Electron Diffraction Technique. Part B: Structural Information from Electron Diffraction for Selected Classes of Compounds. Edited by I. and M. HARGITTAI. (VCH, 1988). Part A: Pp. 563. DM 210·00. ISBN 0 89573 337 4. Part B: Pp. 511. DM 210·00. ISBN 0 89573 292 0.

This is a splendid pair of volumes. The use of electron diffraction to study the geometry of molecules in the gas phase was initiated by Mark and Weirl in 1930, just three years after the experimental verification of the de Broglie relation for the wavelength associated with a moving electron. The technique has since been used steadily and with increasing sophistication, and much important knowledge has been gained about the structure of small molecules. But it has never achieved the massive popularity of X-ray crystallography or NMR. Fewer than a hundred gas ED instruments have ever been built, and at present there are perhaps some twenty experimental centres in the world. The total of over three thousand ED publications increases by a hundred and fifty to two hundred annually.

When W. L. Bragg determined the structure of sodium chloride in 1913, who could have imagined that X-ray crystallography could be developed to determine the structure of proteins? Yet in 1965 Bragg was able to make a drawing of the main polypeptide chain in lysozyme from results obtained by his team at the Royal Institution. Gas ED has been in action for a similar period but has not proved capable of developments so spectacular. Basically the reason is that the diffraction information in crystallography is three-dimensional, whereas with gases the information is one-dimensional. The corresponding Fourier transform represents interatomic distances rather than vectors, and this radial distribution function quickly becomes unmanageable as the size of the molecule increases. Nevertheless, to pick a random example from Part B, the unsymmetrical structure of molecules such as $Zn(C_5H_4SiMe_3)_2$ can be elucidated. The simplest molecules may occur at high temperatures. The chemists who could not accept Bragg's crystal structure for NaCl in 1913, because it contained no identifiable NaCl molecules, might have been comforted had they known of the NaCl monomer as studied at 1130 K by gas ED, although they might still have been puzzled by the presence of dimers.

In investigations of precise geometries or in studies of large-amplitude motions, the essential point to grasp is that there is no single definition of an internuclear distance. There is a clutch of parameters r_e, r_z, r_α, r_g, r_a, r_0, r_s expressing different kinds of potential, thermal or operational parameters. It is the understanding of the relations between these quantities which has led to recent successes in combining gas ED with several kinds of spectroscopy and theoretical calculations, and in obtaining results superior to any single technique.

István and Magdolna Hargittai of Budapest are to be congratulated on having produced these much needed comprehensive volumes on the application of gas ED to stereochemistry. The individual chapters have been written by leading members of the worldwide ED community, and have been blended by the editors into an authoritative and harmonious whole. Part A discusses the development and present capabilities of gas ED, and its combination with other techniques. Part B summarises structural information for many common classes of compound. Curiously neither the extensive indexes nor the list of contents mention the informative foreward by Jerome Karle (a Nobel Laureate for his work on the phase problem in crystallography, but earlier a very significant contributor to gas ED). Neither do they mention the very apposite introduction by Herman Mark himself, the initiator of the whole field in 1930.

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Positron and Positronium Chemistry. Edited by D. M. Schrader and Y. C. Jean. (Elsevier, 1988.) [Pp. 410+xiii.] Dfl. 295·00. ISBN 0 444 43 009 1.

It is many years since a book on this subject has appeared. During the current decade even reviews have been sparse and someone approaching the subject afresh has had to resort to the rather extensive proceedings of the conferences on positron annihilation that have appeared every two or three years. The book is a very timely addition to the chemical literature.

This is a cooperative text but no problems of coherence of the chapters arise since one editor is author, or coauthor, of seven of the eleven chapters. The other editor is similarly involved in three chapters.

All aspects of the subject are treated. The chapter on experimental techniques is concise but up to date and provides an excellent account of current procedures. The longest chapter in the book deals with the theory of positron- and positronium interactions with atoms or molecules. These studies have produced numerous numerical results, but it is disappointing that there is so little experimental data suitable for comparison.

One might hope that the results for gaseous systems would be susceptible to a detailed interpretation. But the rather extensive data, especially on pressure and temperature effects, do not lead to any simple models for the processes involved. A positron–single atom, or molecule, annihilation process is only acceptable at modest pressures. At higher pressures annihilation with clusters of the medium seem to be involved and the decay constant becomes almost independent of pressure. A quantity Z_{eff} can be extracted from these data, which should measure the number of electrons per atom or molecule of the medium susceptible to singlet annihilation with the positron. The values found are often so large that a more complex interpretation will be needed.

Positronium formation in gases would be expected to follow the Ore model, but the experimental yield data only agree with this model at modest pressures.

Much of the rest of the book deals with positronium production in the condensed phase and the relative importance of the Ore and Spur (Mogensen) models for positronium formation in such systems. Despite more than ten years' study this question seems as far as ever from solution. One chapter gives a very satisfactory account of this vexed question. Most of the other topics of investigation, such as the behaviour of liquid mixtures, inhibition and enhancement of positronium formation, are all hard to understand in depth. If these questions were resolved, positron annihilation studies might complement radiation chemistry and yield further information about the early history of the spurs.

Annihilation measurements give useful information about many kinds of phase change, some indeed difficult to detect in other ways. The free space concept seems to provide a useful guide to these changes, but it cannot be said the effects are really understood. Closely related studies cover membranes and interfaces.

Several other, shorter, contributions deal with the applications of slow positron beams and surface investigations and two chapters cover more speculative applications. A promising, very chemical use, is the measurement of complexing constants, where the complex and one of the reactants have closely similar properties.

This is a welcome text, essential to any laboratory interested in this rapidly developing subject.

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Organic Luminescent Materials. By B. M. Krasovitskii and B. M. Bolotin. Translated by V. G. Vopian. (VCH Verlagsgesellschaft, 1988.) [Pp. 340.] DM 198·00. ISBN 3 52726 880 4.

This translation of the second Russian edition, published in 1984, essentially catalogues the syntheses, luminescent properties and various applications of luminescent organic molecules, excluding metal complexes with organic ligands. Since it emphasizes practical uses of luminophors in various fields of science and technology, rather than the photophysical aspects of electronic relaxation, it complements the monographs by Birks, Becker and others.

Following a brief qualitative introduction entitled General Concepts of Luminescence, Part I of the book (seven chapters) details chemical aspects, structures and spectral characteristics of organic luminescent materials classified as aromatic hydrocarbons and derivatives, substituted ethylenes and acetylenes, five- and six-membered heterocyclic compounds, azomethines and azines, carbonyl compounds and naphthalic acids. Part II, consisting of ten chapters, outlines luminescent properties applicable to luminescent dyes, optical brightening agents, organic scintillators, lasers, flaw detection, analytical chemistry, temperature indicators and radiation dosimetry, together with a disappointingly brief chapter on their exploitation in biology and medicine. Useful appendices tabulate reactions for quantitative elemental analysis and, in the style of Berlman's handbook, present absorption and fluorescence spectra for thirty-six compounds of verying structural complexity.

The book is well produced and remarkably free from printing errors, although this reviewer did not check most of the four hundred structural formulae and $>C=0$ appears as $>C=C$ on page 7. There is no evidence that English is the translator's second language (if indeed it is) unless one considers the singularly refreshing use of fluorescence 'killing'. As might be expected, some 60% of the 1100 references are to journals and patent literature published in the U.S.S.R., which provide an indication of Russian research activity in this field up to 1985.

This is not a book for the neophyte seeking exposure to theoretical aspects of internal conversion, intersystem crossing and radiative transition probabilities. It is however to be recommended to the (wealthy) practitioner who understands hypochromic effects, Stokes shifts and hypsofluoric displacements, and is merely researching a luminophoric recipe for a particular application; which is, after all, the authors' stated objective.

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