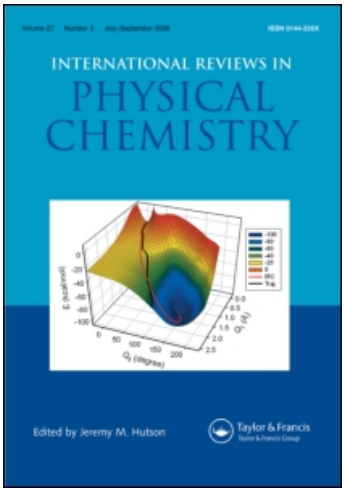

International Reviews in Physical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

Book Reviews

To cite this Article (1983) 'Book Reviews', International Reviews in Physical Chemistry, 3: 3, 393 — 397
To link to this Article: DOI: 10.1080/01442358309353350
URL: http://dx.doi.org/10.1080/01442358309353350

International Reviews in Physical Chemistry (1983), *3* (393–397)

BOOK REVIEWS

R. K. Chang and T. E. Furtak (Eds.) *Surface Enhanced Raman Scattering.* New York: Plenum Press, 1982. 423 pp. $49.50. ISBN 0 306 40907 0.

New phenomena in spectroscopy can certainly be expected to find wide attention and usually the theoreticians come up with a satisfactory explanation after a short while. With the subject of this book the situation is quite different. Although a large number of research teams, particularly in the USA, have studied the phenomenon of Surface Enhanced Raman Scattering (SERS), since it was detected by M. Fleischmann and P. J. Hendra in 1974 at Southampton, the origin of the enhancement is still under controversial discussion.

The editors of this book have collected articles from representatives of twenty research groups active in this field, in which the authors summarize their theoretical ideas or discuss their experimental experiences within the framework of current theories. The contributions are written independently by the different authors, thus avoiding a long delay between delivery and publication in such an active field, but making some repetition of ideas unavoidable. On the other hand, it is instructive to see the varying emphasis of different aspects in the individual contributions.

Nine contributions deal with the theory, eleven present typical experimental examples, including related phenomena like enhanced light scattering from rough surfaces or enhanced luminescence from adsorbed dye molecules. The main and puzzling question today is whether the electromagnetic resonance on a surface of suitable metals—such as those with a dielectric constant which allows surface plasmon excitation, like Ag, Au, Cu, Li or Na—gives a high enough increase of the electric field strength if the surface contains narrowly curved structures, or whether an additional contribution by specific interaction between the metal substrate and the adsorbed molecule, a so-called chemical contribution, is necessary. It appears that all authors agree on the importance of roughness on the surface over dimensions much smaller than the wavelengths of the scattered light, and thereby a locally induced electromagnetic resonance, in order to explain the high enhancement factors of 10^4 to 10^6. Furthermore, most authors seem to assume that a chemical contribution exists. However, the origin of this chemical effect is by no means understood. Another unsolved problem is how to characterize the roughness more precisely.

The book gives an excellent survey of these problems. Its study can be warmly recommended to all those who want to learn what is going on in this exciting new area. It is indispensable for those who are working on such questions, since it not only sums up the scattered information from the literature but also gives a lot of stimulation. And this is needed in a field where the first author, surveying the theoretical ideas in general, ends with the conclusion that '. . . the only unqualified general conclusion I can subscribe to, at this time, is that we need further theoretical and experimental work . . .'.

H. Gerischer
Fritz-Haber-Institut der Max-Planck Gesellschaft
Berlin

K. P. Lawley (Ed.) *Dynamics of the Excited State. Advances in Chemical Physics, Vol. L.* Chichester: J. Wiley, 1982. 667 pp. £35.90. ISBN 0 471 10059 5.

The study of the detailed dynamics of the formation and removal of excited states has assumed great importance in chemical physics, not so much for its importance to lasers but more for the information which it provides about the chemical and physical interactions between molecules. The information has become increasingly detailed as laser and beam experiments have become more sophisticated and powerful.

The present volume contains nine articles in which well-known workers review a series of topics all involving small molecules. The first chapter is a comprehensive review of the study of the excited states of diatomic molecules using laser induced fluorescence, written by (the late) M. A. A. Clyne and I. S. McDermid mainly from an experimental viewpoint.

In Chapter 2, D. S. King gives a thorough account of infrared multiphoton processes, which shows clearly the parallel development of experimental results and theoretical ideas. Surprisingly, the reader has to wait until Chapter 6 for a detailed treatment of the theory of multiphoton infrared processes by M. Quack. This meaty chapter is sandwiched between two accounts of the quenching of metal atoms. The first of these by W. H. Breckenridge and H. Umemoto (Chapter 5) gives a comprehensive summary of experimental results and attempts to relate them to the intermolecular forces involved and to the possible energy disposal processes. In contrast I. V. Hertel (Chapter 7) concentrates on recent results for a few systems, mainly atom + diatomic molecule which we discussed in the light of theoretical calculations of the potential surfaces involved. The following chapter by D. M. Hirst discusses methods for calculating the potential surfaces for excited states and describes the calculations carried out to date without a single diagram to compare theory and experiment.

The remaining three chapters include an excellent and highly readable account by S. R. Leone of the dynamics of photofragmentations; a somewhat algebraic exposition of the possibility of photons as catalysts in laser-induced dissociations by A. M. F. Lau and a discussion by T. A. Brunner and D. Pritchard of how various fitting laws based on simple theoretical models can be used to rationalize rate coefficients for rotationally inelastic collision processes involving the transfer of different amounts of energy.

This volume clearly shows the strengths and weaknesses of multiple authorship. Several chapters are authoritative accounts of areas of considerable current interest which should be available in departmental libraries. Some topics are discussed in more than one chapter, others are missed because they are marginal to an author's particular area. All in all this volume is a worthy fiftieth member of the series 'Advances in Chemical Physics'.

B. A. Thrush
University Chemical Laboratory
Cambridge

G. J. Bullen and D. J. Greenslade. *Problems in Molecular Structure.* London: Pion, 1983. £16. ISBN 0 85086 083 0.

One of the most important aspects of learning is doing. This is particularly so in chemical physics and its neighbouring subjects of physical and theoretical chemistry, for equations often remain remote until they have been used. One way of doing is to work through problems of various difficulty. Another is to adopt the Confucian manner, and to learn by working through examples already solved and set out by others. The difficulty with the latter approach is finding suitable material. The literature is one source, but it needs an acute eye and a good familiarity with the field to spot the best material. An alternative is to have the literature pre-selected, pre-digested, and served up ready cooked. This book does exactly that.

Problems in Molecular Structure consists of seven chapters which identify various aspects of molecular structure, including symmetry, diffraction, vibration-rotation spectroscopy, electronic properties, nuclear spectroscopy, mass spectrometry and structure and energy. It should be noted that the 'structure' of the title is interpreted as various aspects of the determination of structure by the principal techniques of physical chemistry, and not as molecular orbital calculations and related aspects of quantum chemistry.

The chapters are divided into twenty-four sections which have been contributed by twenty-five experts. Some measure of the length of time it has taken for the editors to assemble the contributions is that Charles Coulson (d. 1974) is among them. The concentration on expertise rather than uniformity of presentation is sensible at this level, and in reading through the contributions one cannot fail to appreciate the advantage of standing beside the horse's mouth. This, in fact, is the strength of the book, because it gives the opportunity to listen to

an expert thinking more slowly than is normally the case in the conventional literature.

In the twenty-four sections we meet typical problems arising in X-ray (Bullen), electron (Beagley), and neutron (Speakman) diffraction, magnetic resonance (Whiffen, Lucken), optical activity (Mason), dipole moment (Buckingham), bond energy studies (Skinner), as well as in many others. The level is high, and whilst I doubt whether undergraduates will find it exactly what they need, their lecturers should find the book a mine of information to draw on when compiling their own problems and solutions.

I have one or two notes of minor criticism. One is the presentation: it is often quite difficult to see where the question ends and the solution begins. More importantly, some solutions do not give much help in finding strategies for answering similar questions: the solutions begin with an assertion rather than with the establishment of an attitude. These, however, are minor points, and should not detract from the usefulness of this valuable book.

P. W. Atkins
Lincoln College
Oxford

G. A. Somorjai. *Chemistry in Two Dimensions: Surfaces.* Cornell University Press, 1981. 575 pp.

The George Fisher Baker Non-Resident Lectures at Cornell University have led to the publication of many excellent monographs. In this volume one of the leading exponents of the application of modern surface science methods to the chemistry of solid surfaces presents a perspective of surface chemistry from the viewpoint of his own research interests. The result is not a comprehensive overview of surface chemistry but then a comprehensive survey of such a richly diverse subject would inevitably be either superficial or exhausting. Instead, we have an authoritative yet enjoyably readable account of some of the most exciting developments in the study of solid surfaces—those based on techniques capable of probing the geometry, electronic structure, energetics and dynamics of surface layers and chemical processes at surfaces. The explosive growth of surface science has generated an enormous research literature but there has been a dearth of texts to inculcate a sense of its purpose and dynamism. Somorjai's book fills this gap admirably. It will be invaluable to the novice and to the experienced research worker with its wealth of information and discussion supported by some 150 pages of referenced experimental data.

Starting with a general discussion of the importance of interfaces the emphasis of the book quickly develops towards the study of single crystal surfaces, particularly of metals. The reasons for this are made clear through a survey of the 'tools of the surface scientist's trade', where techniques for structural investigation such as low energy electron diffraction (LEED), ion scattering and electron energy loss spectroscopy, which require well ordered surfaces, and a variety of other physical techniques (e.g., photoemission, secondary ion mass spectrometry) are outlined. The factors affecting segregation at surfaces are then considered, followed by an account of the crystallography of clean single crystal surfaces and of the relaxations and reconstructions which frequently occur.

The scene has then been set for an extensive review of the structures of adsorbed monolayers, both chemisorbed and physically adsorbed, with extensive tabulations of experimental results. There is a strong emphasis here on low energy electron diffraction investigations, but the need for combinations of techniques is illustrated by a number of important examples, e.g., the use of vibrational spectroscopy (EELS) with LEED to identify ethylidyne structures formed from acetylene and from ethylene at Pt(111) surfaces. This section is followed quite naturally by a discussion of the nature of the bonding to the surface.

Kinetic aspects of surface chemistry are introduced by reference to energy transfer in gas–surface interactions and the detailed information that molecular beam methods can provide. Then a treatment of the principles of catalysis by surfaces is accompanied by a massive compilation of catalytic kinetic data for reactions at metal surfaces. The theme of catalysis is pursued through the remaining chapters. These deal with specialized topics to which Somorjai

has made major contributions: hydrocarbon conversion at platinum surfaces and the role of surface steps, the catalytic hydrogenation of carbon monoxide, and, of a rather different character, photochemical surface reactions in aqueous media and the photochemical production of hydrogen at strontium titanate surfaces.

Selectivity is an important concept in catalysis. Some readers may well feel that the author has practised selectivity too much in the scant treatment afforded to several very active fields of research on solid surfaces. However, Somorjai has very successfully drawn together the themes of catalysis and modern surface science, pointing to past achievement and showing us an exciting prospect. It is a valuable perspective.

J. Pritchard
Queen Mary College, London

J. W. Akitt. *NMR and Chemistry* (2nd edn). London: Chapman and Hall, 1983. 263 pp. £7.95. ISBN 0 412 24020 3.

NMR is an unusually difficult subject to teach at undergraduate level; it has relatively few points of contact with other spectroscopic techniques, and yet a basic grasp of its principles and applications is an important part of a chemical education. Any author who sets out to provide a non-mathematical account of the whole area of NMR has taken on a difficult task, and deserves a sympathetic hearing; an approach which also concentrates throughout on chemical applications is doubly welcome.

Unfortunately, despite these admirable aims, it is difficult to give more than a guarded welcome to this book. Although sound on topics such as spectral analysis and interpretation (well covered in existing texts), the accounts of more advanced topics are frequently unclear and not infrequently misleading. Minor chemical slips ('methyl nitrate' for CH_3NO_2, tetravalent oxygen, etc.) will not detain the sensible student, but the descriptions of the behaviour of nuclear magnetism during various types of experiment are likely to cause considerable confusion.

One central problem is the decision to dispense with both the Bloch equations and the rotating frame of reference. This leads to several pages of opaque algebra and inverted logic in the discussion of FTNMR lineshapes, and to some all but impenetrable vector diagrams. Indeed at several points (for example in describing spin echoes) the author gives up the unequal struggle and uses a rotating reference frame without explanation. The eccentric choice of representing $\boldsymbol{B}_0$ along a horizontal $-z$ axis does not help. Difficulties also arise from the use of hand-drawn spectra, making near-nonsense of illustrations of the effects of time-averaging and exponential weighting on signal-to-noise ratio. Less mathematical topics also suffer; for example the introduction of the nuclear Overhauser effect as an INDOR-type population perturbation is thoroughly misleading.

The new chapter on modern extensions of NMR, and the willingness throughout to mention recent work where appropriate, offer the student a welcome taste of current developments. More leading references here would have been useful, particularly as some of the explanations are incorrect; indeed at one point two quite different heteronuclear 2D NMR experiments become inextricably entangled. The redeeming feature of this book is, however, its extensive use of chemical examples, particularly in the enlarged final chapter. These case studies form a useful source of teaching material, covering a wide range of different nuclei in many different areas of chemistry. Although not recommendable for undergraduate use, the book may well prove useful to teachers of NMR.

G. A. Morris
Department of Chemistry
The University of Manchester

J. Ościk. *Adsorption.* Chichester: Ellis Horwood (John Wiley), 1982. xv + 206 pp. £22.50.

I. L. Cooper (University of Newcastle upon Tyne) has translated this concise text from Polish, first published by PWN, Warsaw in 1979. The author, from the Maria-Curie-Sklodowska University, Lublin, has set out to produce a coherent account of adsorption covering, as very few monographs have done previously, the liquid–gas, solid–gas, solid–liquid, liquid–liquid interfaces. In so far as the various thermodynamic treatments of such interfaces are concerned, the result is a clear success. Lucid accounts are given of all the principal theories of adsorption from Polanyi's 'potential theory' through to the Dubinin–Raduschkevitch treatment and beyond. Adsorption at heterogeneous surfaces and from multicomponent systems are also neatly handled.

But the book almost completely neglects the experimental approach to the study of the structure and bonding of adsorbed phases. Even some of the more elementary, but important, spectroscopic tools, such as infra-red spectroscopy pioneered by Eischens and by Sheppard more than a quarter of a century ago are omitted; and there is no mention of any of the various surface diffraction and photoelectron techniques that have been widely and effectively used over the past decade. Moreover, two-dimensional phase transitions, which have spawned so much adventurous work in condensed-matter physics and chemistry of late, at so-called homotattic or energetically uniform surfaces are not touched upon.

Nevertheless, despite these errors of omission, and the fact that many of the illustrative examples of observed isotherms are taken from relatively ancient publications, the book can be warmly recommended as a teaching text for undergraduate courses.

J. M. Thomas
University Chemical Laboratory
Cambridge